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DARPA - Advanced Composite Materials

Annual Presentation

November 19-20, 1992

University of Florida
Gainesville, FL 32611

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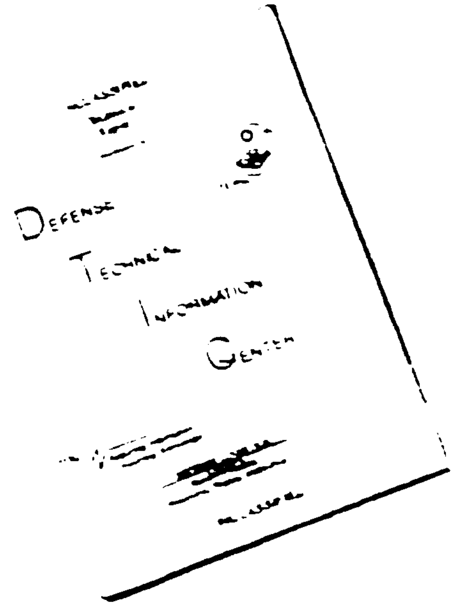

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DARPA - Composites Annual Review
November 19-20, 1992

University of Florida, Gainesville, Florida

Thursday, November 19

1:30-1:45	Opening Remarks - Drs. Wilcox, Coblenz, Fishman
1:45-2:00	Overview - Reza Abbaschian
2:00-2:50	SiC Fibers - Chris Batich, Michael Sacks, Bill Toreki
2:50-3:20	Mullite Fibers - Joseph Simmons, Anthony Brennan
3:20-3:50	CVD Approaches to Composites - Tim Anderson
3:50-4:00	Break
4:00-6:00	Poster Presentation and Refreshments - Students

Friday, November 20

8:00-8:50	Intermetallic Composites - Michael Kaufman, Reza Abbaschian
8:50-9:40	Ceramic Composites - David Clark, Michael Sacks
9:40-10:10	Tapecast Laminated Composites - Jack Mecholsky
10:10-10:30	Break
10:30-11:15	Future Plan and General Discussions - R. Abbaschian
11:15-12:00	Summary and Comments
12:00-1:30	Lunch
1:30	Informal Subgroup Discussions and Tour of the Facilities

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List of Poster Presentations

Arredondo Room - 4:00 pm to 6:00 pm

Fiber Synthesis/Coating

1) "Atomic Layer Epitaxy"
   R. Aparicio,* E. Allen, J. Wolan, and T.J. Anderson
2) "Chemical Vapor Infiltration"
   R. Aparicio, E. Allen,* J. Wolan, and T.J. Anderson
3) "Chemical Vapor Deposition of TiC_x on Refractory Substrates"
   R. Aparicio, E. Allen, J. Wolan,* and T.J. Anderson
4) "Chemical Vapor Infiltration and Atomic Layer Deposition of TiC on Ceramic Substrates"
   R. Aparicio, E. Allen, J. Wolan, and T.J. Anderson*
5) "Sol-Gel Processing of Continuous Mullite Based Fibers"
   S. Al-Assafi,* T. Cruse, T. Miller, A.B. Brennan, and J.H. Simmons
6) "Sol-Gel Processing of Continuous Mullite Based Fibers"
   S. Al-Assafi, T. Cruse,* T. Miller, A.B. Brennan, and J.H. Simmons
7) "Polymer-Derived Silicon Carbide Fibers with Low Oxygen Content and Improved Thermomechanical Stability"
   W. Toreki, C.D. Batich, M.D. Sacks, M. Saleem,* G.J. Choi, and A. Morrone

Microwave Processing

8) "Microwave Processing of High-Performance Ceramics and Composites"
   D.E. Clark, Z. Fathi,* A.D. Cozzi, D.C. Folz, I. Ahmad, S. Al-Assafi, A.S. De', and R.C. Dalton
9) "Microwave Processing of Sol-Gel-Derived Glass-Ceramics for High Temperature Composite Matrices"
   A.D. Cozzi,* Z. Fathi, and D.E. Clark

Ceramic Matrix Composites

10) "Fabrication of Mullite and Mullite-Based Composites by Transient Viscous Sintering (TVS) and Pressure-Assisted Transient Viscous Sintering (PATVS)"
    N. Bozkurt, G.W. Scheiffele,* Y.J. Lin, A. Ulicny, and M.D. Sacks
11) "Fabrication of Composites with Low Dielectric Constant Using Microcomposite Particles"
    R. Raghunathan,* I.Y. Park, G.W. Scheiffele, and M.D. Sacks
12) "Processing, Microstructure and Properties of SiAlONs Prepared from Microcomposite Particles"
    A. Bagwell, R. Raghunathan,* and M.D. Sacks
13) "Fabrication of SiC-Based Composites by Reactive Infiltration of Metals (RIM)"
    K. Wang,* G.W. Scheiffele, P.J. Sanchez-Soto, and M.D. Sacks

* Indicates Presenter

Intermetallic Matrix Composites

14) "Processing of Compositionally Tailored Silica-Free $MoSi_2$/SiC Composites"
S. Jayashankar,* A. Costa e Silva, and M. Kaufman
15) "Phase Relations in Some Systems Relevant to $MoSi_2$ Processing"
A. Costa e Silva,* S. Jayashankar, and M. Kaufman
16) "Modelling and Design of Toughened Composites"
L. Xiao, M. Somerday,* and R. Abbaschian
17) "Microstructures and Properties of $MoSi_2$/Nb Coated and Uncoated Interfaces and Their Effects on Toughness"
L. Xiao* and R. Abbaschian
18) "Toughening and Strengthening of $MoSi_2$ with SiC Whiskers and Ductile Reinforcement"
L. Xiao* and R. Abbaschian
19) "Fabrication of Toughened Composites via Reactive Hot Compaction and In-situ Coating"
H. Doty,* L. Lu, A. Gokhale, and R. Abbaschian
20) "Development and Characterization of Interface Coatings in NiAl Matrix Composites"
P. Krishnan* and M. Kaufman
21) "Fiber-Reinforced $TaTiAl_2$ Alloy Composites"
I. Hwang* and R. Abbaschian

Mechanical Behavior

22) "Optimization of Creep and Fracture Properties by Microstructure Design"
B. De Aragao,* J.R. Castillo, and F. Ebrahimi
23) "Fracture Energy Anisotropy of Single Crystals"
L. Kalwani* and F. Ebrahimi
24) "Toughening by Metallic Lamina in Tape Casting Nickel/Alumina Composites"
Z. Chen* and J.J. Mecholsky Jr.
25) "Fracture of CVD Diamond Films on Silicon"
Y.L. Tsai* and J.J. Mecholsky Jr.

Other Contributed Posters on New Processing Technologies

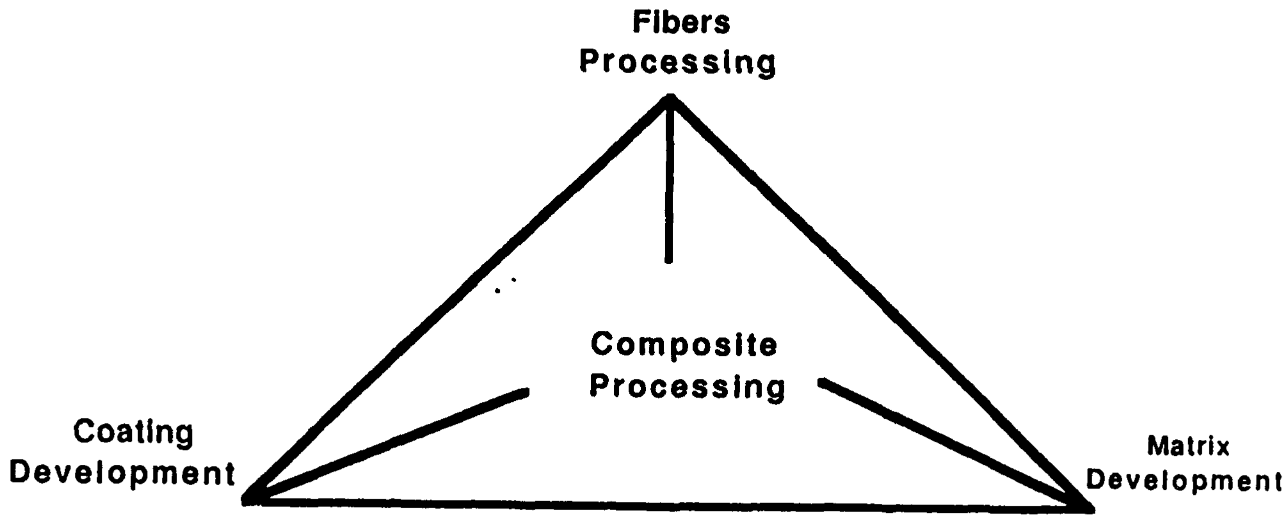
26) "Surface Modification of $BaTiO_3$ Particles Via Oxalic Acid, Polyethyleneimine in Aqueous Systems"
R.E. Chodelka* and J.H. Adair
27) "Electrothermal Synthesis of $BaTiO_3$ Thin Films at 55° C"
S. Venigalla,* P. Bendale, T. Tsukada, J.R. Ambrose, and J.H. Adair
28) "Glycothermal Synthesis of α-Al_2O_3 Particles at Ultra-Low Temperature"
S.B. Cho,* S. Venigalla. R.E. Chodelka, and J.H. Adair
29) "Monodispersed Nanosize Pt Particles Using Microemulsion Technique"
V. Nagabushnam* and J.H. Adair

* Indicates Presenter

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

PROGRAM OVERVIEW

Reza Abbaschian



MSE — UNIVERSITY OF FLORIDA

Program Objective

Provide a fundamental understanding of the processing science and technology necessary for cost-effective fabrication of ceramic-matrix and intermetallic-matrix composites with superior mechanical properties in high temperature and oxidizing environments. The composites are intended for use as structural materials for advanced aerospace applications at temperatures exceeding 1200°C.

Critical Property Requirements

- High stiffness
- High strength
- High toughness
- Low density
- Thermal shock resistance
- Creep resistance
- Fatigue resistance
- Environmental stability
- Structural stability

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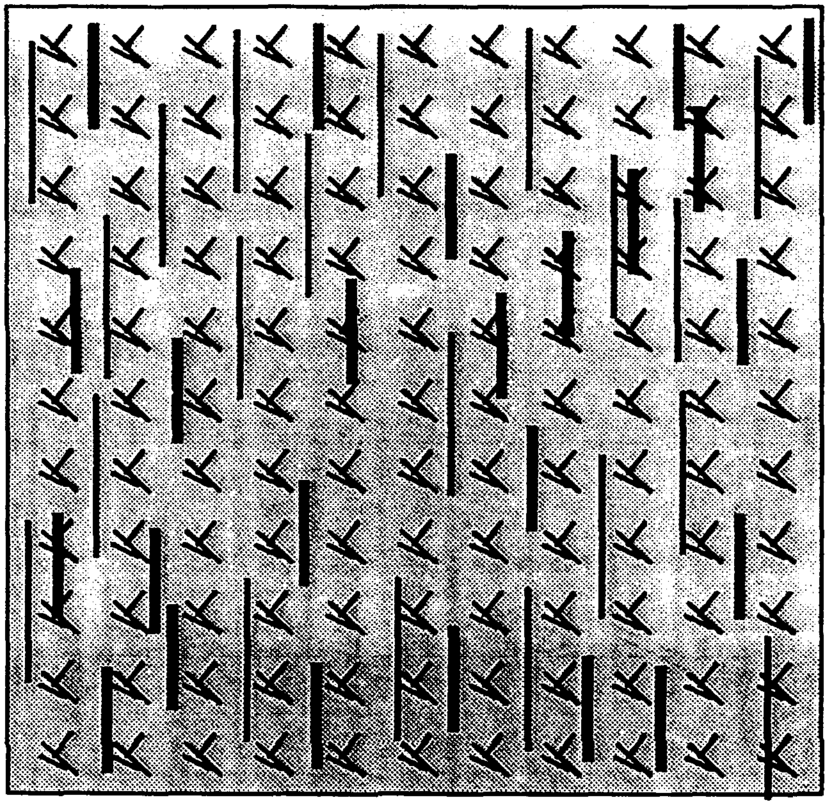
High Temperature Composite Needs

- Reinforcement materials with desired geometry, property and stability
- Matrix materials with appropriate properties and stability
- Interfacial control between reinforcement and matrix during processing and service
- CTE mismatch adjustments
- Cost effective processing and consolidation techniques

HYBRID COMPOSITES



COMPOSITE ELEMENTS

Environmentally Stable Matrix With Fine Dispersions For CTE Matching

Dispersions For Increased Strength and Creep Resistance

High Strength, High Aspect Ratio Reinforcing Phase For High Temperature Strength

Ductile Phase Reinforcement For Low Temperature Toughness

Interfacial Tailoring For Optimum Mechanical and Chemical Stability

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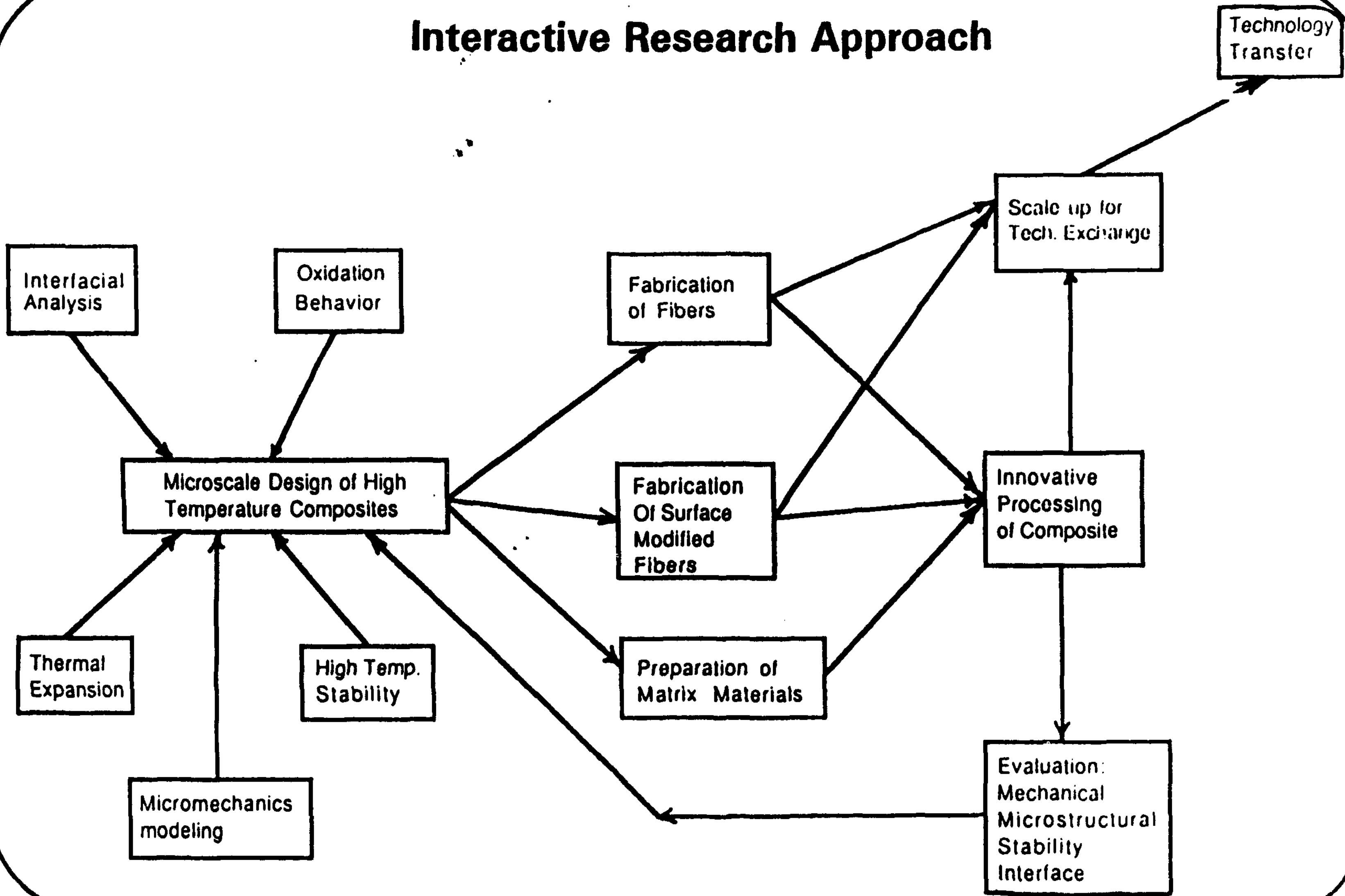
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Interactive Research Approach



MSE — UNIVERSITY OF FLORIDA

Major Thrusts of the Program

- A fundamental approach to microscale design of high temperature composites with tailored mechanical, chemical and physical properties.
- Development and scientific understanding of processes for the fabrication of refractory ceramic fibers with improved high temperature mechanical properties and stability.
- Development and scientific understanding of processes and properties necessary to control the chemicl and mechanical integrity of the matrix/reinforcement.
- Development of innovative methods for the preparation of dense intermetallic-matrix and ceramic-matrix composites containing fiber and/or whisker reinforcement.
- Technology transfer.

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Current Program Emphasis Areas

- **FIBER FABRICATION**
  - Mullite-based Fibers - A.B. Brennan and J.H. Simmons
  - SiC-based Fibers - C.D. Batich, M.D. Sacks, and W. Toreki
- **COATINGS**
  - Chemical Vapor Deposition of Refractory Carbides - T.J. Anderson
- **COMPOSITE FABRICATION**
  - Intermetallic Matrix Composites - R. Abbaschian and M.J. Kaufman
  - Ceramic Matrix Composites - M.D. Sacks
  - Microwave Processing of Composites - D.E. Clark
  - Laminated Ceramic/Metal Composites - J.J. Mecholsky, Jr.

LIST OF PUBLICATIONS

1. K.R. Venkatachari, L.T. Moeti, M.D. Sacks, and J.H. Simmons, "Preparation of Mullite-Based Fibers by Sol-Gel Processing," Ceram. Eng. Sci. Proc., 11 (9-10) pp. 1512-1525 (1990).

2. S-M. Sim and D.E. Clark, "Preparation of Zirconia Fibers by the Sol-Gel Method," Ceram. Eng. Sci. Proc., 10 (9-10) pp. 1271-1282 (1989).

3. S-M. Sim, A. Morrone, and D.E. Clark, "Processing and Microstructure of Y-TZP/Al_2O_3 Fibers," Proceedings of the 14th Annual Conference on Composites and Advanced Ceramics held on January 14-17, 1990 in Cocoa Beach, FL. Published in Ceram. Eng. Sci. Proc., 11 (9-10) pp. 1712-1728 (1990).

4. S-M. Sim, "Processing and Microstructural Characterization of Alumina-Dispersed Zirconia Fibers," Doctoral dissertation, University of Florida (1990).

5. W. Toreki and C.D. Batich, "Effects of Molecular Weight and Cross-Linking on Two Preceramic Polymers," presented at the American Chemical Society National Meeting in Miami Beach, FL, September 1989. Published in Polymer Preprints, 30 (2) pp. 237-238 (1989).

6. W. Toreki, C.D. Batich, M.D. Sacks, and A.A. Morrone, "Synthesis and Applications of a Vinylsilazane Preceramic Polymer," Ceram. Eng. Sci. Proc., 11 (9-10) pp. 1371-1386 (1990).

7. W. Toreki, N.A. Creed, and C.D. Batich, "Silicon-Containing Vinyl Polymers as Precursors to Ceramic Materials," Polymer Preprints, 31 (2) pp. 611-612 (1990).

8. W. Toreki, "Polymeric Precursors to Ceramics-A Review," feature article in Polymer News, 16 (1) pp. 6-14 (1991).

9. W. Toreki, C.D. Batich, and G.J. Choi, "High Molecular Weight Polycarbosilane as a Precursor to Oxygen-Free SiC Fibers," presented at The ACS National Meeting in New York, August, 1991. Published in Polymer Preprints, 32 (2) (1991).

10. W. Toreki, C.D. Batich, M.D. Sacks, M. Saleem, G.J. Choi, and A.A. Marrone, "Polymer-Derived Silicon Carbide Fibers with Low Oxygen Content and Improved Thermomechanical Stability," to be published in the Journal of Composites Science and Technology.

11. W. Toreki, C. Batich, M.D. Sacks, M. Saleem, and G. Choi, "Polymer-Derived Silicon Carbide Fibers with Improved Thermomechanical Stability," pp. 761-769 in Better Ceramics Through Chemistry V, edited by M.J. Hampden-Smith, W.G. Klemperer, and C.J. Brinker, Mat. Res. Soc. Symp. Proc., Vol. 271, Materials Research Society, Pittsburgh, PA (1992).

12. W. Toreki, G.J. Choi, C. Batich, M.D. Sacks, and M. Saleem, "Polymer-Derived Silicon Carbide Fibers with Low Oxygen Content, Ceram. Eng. Sci. Proc., 13 (9-10) pp. 198-208 (1992).

13. R. Aparicio, J.L. Ponthenier, F. Hong, and T.J. Anderson, M.D. Sacks, and G. Johnson, "Chemical Vapor Deposition on TiC_x on Al_2O_3 Substrates," Ceram. Eng. Sci. Proc., 10 (9-10) pp. 1462-1471 (1989).

14. M.S. Dariel, R. Aparicio, T.J. Anderson, and M.D. Sacks, "CVD of TiC_x on Refractory Materials," Proc. 11th International Conference on Chemical Vapor Deposition, Seattle, WA (1990).

15. R. Aparicio, E.F. Allen, J. Anderson, and M.D. Sacks, "CVD of TiC_x on Single Crystal Al_2O_3," pp. 145-152 in Advanced Composites Materials, Ceramic Transactions, Vol. 19, edited by M.D. Sacks, American Ceramic Society, Westerville, OH (1991).

16. H.-W. Lee and M.D. Sacks, "Pressureless Sintering of Al_2O_3/SiC Whisker Composites," Ceram. Eng. Sci. Proc., 10 (9-10) pp. 720-729 (1989).

17. H.-W. Lee and M.D. Sacks, "Pressureless Sintering of SiC-Whisker-Reinforced Al_2O_3 Composites: I, Effect of Matrix Powder Surface Area," Journal of the American Ceramic Society, 73 (7) pp. 1884-1893 (1990).

18. H.-W. Lee and M.D. Sacks, "Pressureless Sintering of SiC-Whisker-Reinforced Al_2O_3 Composites: II, Effect of Sintering Additives and Green Body Infiltration," Journal of the American Ceramic Society, 73 (7) pp. 1894-1900 (1990).

19. M.D. Sacks, N. Bozkurt, and G.W. Scheiffele, "Transient Viscous Sintering of Mullite and Mullite-Matrix Composites," pp. 111-123 in Advanced Composite Materials, Ceramic Transactions, Vol. 19, edited by M.D. Sacks, American Ceramic Society, Westerville, OH, (1991).

20. M.D. Sacks, M.S. Randall, G.W. Scheiffele, and J.H. Simmons, "Processing of Silicate Glass/Silicon Nitride Composites with Controlled Microporosity," pp. 407-420 in Advanced Composite Materials, Ceramic Transactions, Vol. 19, edited by M.D. Sacks, American Ceramic Society, Westerville, OH, (1991).

21. M.D. Sacks, G.W. Scheiffele, N. Bozkurt, R. Raghunathan, and A.E. Bagwell, "Processing of Composite Powders: Fabrication of Ceramics and Composites by Viscous Sintering and Transient Viscous Sintering," pp. 557-575 in Chemical Processing of Advanced Materials, edited by L.L. Hench, J. West, and D.R. Ulrich, Wiley, NY (1992).

22. M.D. Sacks, G.W. Scheiffele, N. Bozkurt, and R. Raghunathan, "Fabrication of Ceramics and Composites by Viscous and Transient Viscous Sintering of Composite Particles," pp. 437-455 in Ceramic Powder Science IV, Ceramic Transactions, Vol. 23, edited by S.-I. Hirano, G.L. Messing, and H. Hausner, American Ceramic Society, Westerville, OH (1991).

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25. L. Lu, A.B. Gokhale, M.J. Kaufman, and R. Abbaschian, "Niobium Aluminide Matrix Composites Produced by the Reactive Hot Compaction of Elemental Powders," in Powder Metallurgy: Key to Advanced Materials Technology, ASM, 1990, pp. 32-36.

26. A.B. Gokhale, L. Lu, and R. Abbaschian, "Interface Reactions in Melt Infiltration Processed Intermetallic Matrix Composites," in Solidification of Metal Matrix Composites, P. Rohatgi, Ed., 1990, pp. 115-131.

27. R.E. Erickson, D.R. Baker, and M.J. Kaufman, "Microstructural Development and Second Phase Toughening of $NbAl_3$," Proceedings of the 3rd Annual HITEMP Review, NASA Conference Publication 10051, (1990) p.22-1.

28. L Lu, A.B. Gokhale, and R. Abbaschian, "In-situ Formation of an Alumina Interface Coating in Reactively Synthesized $NbAl_3$-Nb Composites," Materials Science and Engineering, A133, pp. 11-23 (1991).

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32. L. Xiao and R. Abbaschian, "On the Strength and Stiffness of Ductile Phase Reinforced $MoSi_2$ Composites," in Advanced Metal-Matrix Composites for Elevated Temperatures, ASM International, 1991, pp. 21-31.

33. L. Xiao and R. Abbaschian, "The Role of Matrix/Reinforcement Interfaces in the Fracture Toughness of Ductile Phase Reinforced $MoSi_2$ Composites," to be published in Advanced Metal-Matrix Composites for Elevated Temperatures, Proceedings of 1991 TMS Fall Meeting, Cincinnati, OH, October, 1991.

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37. L. Xiao and R. Abbaschian, "Interfacial Modification in Nb/$MoSi_2$ Composites and Its Effects on Fracture Toughness," Journal of Materials Science and Engineering, 1992, Vol. A155, pp. 135-145.

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41. L. Xiao and R. Abbaschian, "Flow Behaviors of Constrained Ductile Phases," to appear in Metall. Trans. A.

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44. S. Jayashankar, I. Harangazo, Y.S. Kim, and M.J. Kaufman, "Powder Processing of $MoXi_2$," (in preparation).

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52. A.S. Dé, "Ultra-Rapid Sintering of Alumina with Microwave Energy at 2.45 GHz," Master's Thesis, University of Florida (1990).

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77. R.B. Erickson and M.J. Kaufman, "Microstructures and Phase Relationships in Ternary Aluminum-Niobium-Vanadium Alloys," (in preparation).

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79. M.D. Sacks, R. Raghunathan, I.Y. Park, and G.W. Scheiffele, "Processing and Properties of Glass/Ceramic Composites with Low Dielectric Constant Prepared from Microcomposite Particles," to be published in Advances in Ceramics.

80. Z. Chen and J.J. Mecholsky, Jr., "Toughening by Metallic Lamina in Metal/Alumina Composites," for publication in the Journal of The American Ceramic Society.

81. Z. Chen and J.J. Mecholsky, Jr., "Damage Tolerant Laminated Composites In Thermal Shock," for publication in the Acta Metallurgica et Materialia.

82. Z. Chen and J.J. Mecholsky, Jr., "Control of Strength and Toughness of Ceramic/Metal Laminates Using Interface Design," for publication in the Journal of Materials Research.

Patent Disclosures and Applications

1. "Polycarbosilane Preceramic Material," W. Toreki and C.D. Batich, August, 1989, patent disclosure.

2. "Polysilazane Preceramic Polymer via Free-radical Initiation," W. Toreki and C.D. Batich, August, 1990, patent disclosure.

3. "SiC Fibers Having Low Oxygen Content and Methods of Preparation", W. Toreki and C.D. Batich. Patent application approved for issue by U.S. Patent Office, July, 1992.

4. "Alumina- or Alumina/Zirconia-Silicon Carbide Whisker Ceramic Composites and Methods of Manufacture," M.D. Sacks and H.W. Lee, U.S. Patent No. 5,009,822, April 23, 1991.

5. "Silica-Coated Composite Powder," M.D. Sacks and C.S. Khadilkar, U.S. Patent Application Serial No. 07/714/438.

6. "Pressureless Sintering of (Si-O)-Containing Ceramics and Composites," M.D. Sacks, U.S. Patent Application Serial No. 07/714,853.

7. "Method for Processing of Mullite and Mullite-Based Composites by Transient Viscous Sintering," M.D. Sacks et al. (in preparation).

8. "Method for Fabrication of Improved Reaction-Bonded Silicon Carbide," M.D. Sacks, K. Wang, and G.W. Scheiffele, patent disclosure.

9. An 'In-Situ' Coating Process of Reinforcements Used in Reactively Synthesized Metal, Intermetallic, and Ceramic Matrix Composites," L. Lu, A.B. Gokhale, and R. Abbaschian, U.S. Patent Application Serial No. 07/794,944.

10. "Combustion Synthesis of Materials Using Microwave Energy," D.E. Clark, I. Ahmad, and R.C. Dalton, U.S. Patent Application Serial No. 351,059, Filed 5/12/89.

11. "SiC Fibers Having Low Oxygen Content and Methods of Preparation", W. Toreki and C.D. Batich, Divisional Patent containing supplemental material, Application filed May, 1992.

12. "SiC Fibers with Controlled Carbon and Oxygen", C.D. Batich, W. Toreki, M.D. Sacks, and G. Choi, patent application.

13. "A New Method for the Fabrication of Silica-Free, CTE Matched, Ductile Phase Reinforced Silicide Matrix Composites," S. Jayashankar and M.J. Kaufman, patent disclosure.

14. "Tailored Silicide/Silicon Carbide Composites by Mechanical Alloying and *In-Situ* Displacement Reactions," S. Jayashankar and M.J. Kaufman, patent disclosure.

DARPA

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

POLYMER-DERIVED SILICON CARBIDE FIBERS WITH LOW OXYGEN CONTENT AND IMPROVED THERMOMECHANICAL STABILITY

Principal Investigators: C.D. Batich and M.D. Sacks

OUTLINE

- **BACKGROUND**
  Nicalon™ Fibers
  Other SiC fibers

- **OBJECTIVE**

- **RESULTS**
  UF SiC Fibers

- **FUTURE DIRECTIONS**
  R & D Needs

NICALON™ "SILICON CARBIDE" FIBERS

Processing: Melt Spinning of Polycarbosilane, Oxygen Cross-Linking, Pyrolysis

Structure: Continuous, Fine-Diameter Fibers; Weakly Crystalline, Fine-Grained SiC; Large Excess of Oxygen and Carbon

Properties: High Tensile Strength, High Rupture Strain, Low Modulus, Poor Thermal Stability

CONTINUOUS SILICON CARBIDE FIBERS (Yajima et al.)

$$\text{Polydimethylsilane} \xrightarrow[\text{Argon/Autoclave}]{450\text{-}470^\circ\text{C}/14\ \text{h}} \text{Polycarbosilane} \xrightarrow{280^\circ\text{C Vacuum}} \text{Polycarbosilane}\ (M_n < 1750) \xrightarrow{350^\circ\text{C}/N_2} \text{Melt Spun Fibers} \xrightarrow{150^\circ\text{C}/5\ \text{h/Air}} \text{Oxygen-Crosslinked Fibers} \xrightarrow{1000\text{-}1200^\circ\text{C/Inert Atmosphere}} \text{"SiC" Fibers}\ (8\text{-}15\ \text{wt\% Oxygen})$$

DEGRADATION OF NICALON FIBERS

- Reactions Involving SiO_2 and Excess C
- Large Weight Losses - Volatilization of CO, SiO
- Development of Porosity and Growth of Flaws
- Rapid Grain Growth

FINE-DIAMETER SILICON CARBIDE FIBERS

Organosilicon Polymer-Derived

Hi-Nicalon (Nippon Carbon Co.)[1] - melt spun, radiation-cured, low oxygen content, excess carbon, good thermal stability, high tensile strength, improved elastic modulus

Lipowitz et al.[2] (Dow Corning Corp.) - melt spun, oxygen cross-linking and boron doping, near stoichiometric SiC, good thermal stability, high tensile strength and high elastic modulus, heterogeneous microstructure, continuous?

SiC Powder-Derived

Frechette et al.[3] (Carborundum Co.) - powder/polymer melt extrusion, larger fiber diameter ($\geq 25\ \mu m$), near stoichiometric SiC, good thermal stability, low tensile strength, high elastic modulus

Silverman et al.[4] (Du Pont Co.) - slurry-processed (with organosilicon binder), larger fiber diameter ($\geq 25\ \mu m$), near stoichiometric SiC, good thermal stability, low tensile strength, high elastic modulus

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1. M. Takeda et al., Ceram. Eng. Sci. Proc., 13 [7-8] 209-217 (1992).
2. J. Lipowitz et al., Ceram. Eng. Sci. Proc., 12 [9-10] 1819-1831 (1991).
3. F. Frechette et al., Ceram. Eng. Sci. Proc., 12 [7-8] 992-1006 (1991).
4. L.A. Silverman et al., J. Appl. Polymer Sci.: Appl. Polymer Symp., 47 99-109 (1991).

Objective

- Synthesis of continuous SiC fibers with small diameter, high tensile strength, and good thermomechanical stability

Approach

- Fabricate SiC fibers with low oxygen content
- Dry spinning of organosilicon polymers *without* oxidative or irradiative curing step

CONTINUOUS SILICON CARBIDE FIBERS (Toreki et al.)

Polydimethylsilane

↓ Heat Treatment

Polycarbosilane

↓ Solution/Filtration
Precipitation/Filtration
60°C/Vacuum

Polycarbosilane (M_p = 5,000-10,000)

↓ Solvent, Spinning Aids, etc.

Spinning Dope

↓ Dry Spinning
Ambient Atmosphere

Green Fibers

↓ Pyrolysis (~1000°C)

"SiC" Fibers (<2 wt% Oxygen)

KEY PROCESSING VARIABLES

Polycarbosilane Molecular Weight

MW < 5,000	Highly soluble, but melts; Low ceramic yield
MW > 10,000	Does not melt, but insoluble; High ceramic yield
MW ≈ 5,000-10,000	Does not melt, highly soluble; High ceramic yield

Polymer/Solvent Ratio in Spinning Dope

Excess of solvent - fibers stick together

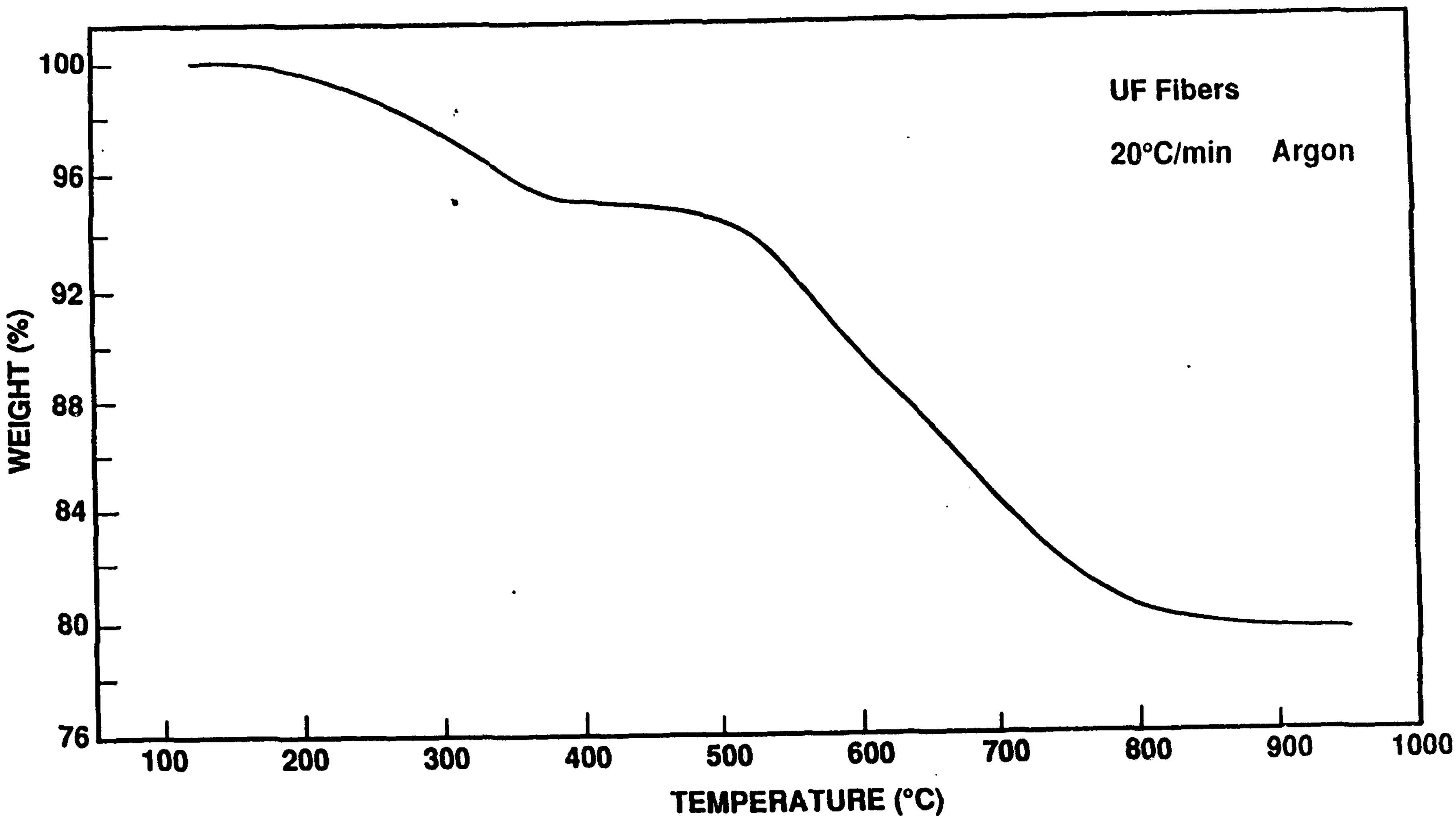
Deficiency of solvent - difficult to extrude, rough fiber surfaces

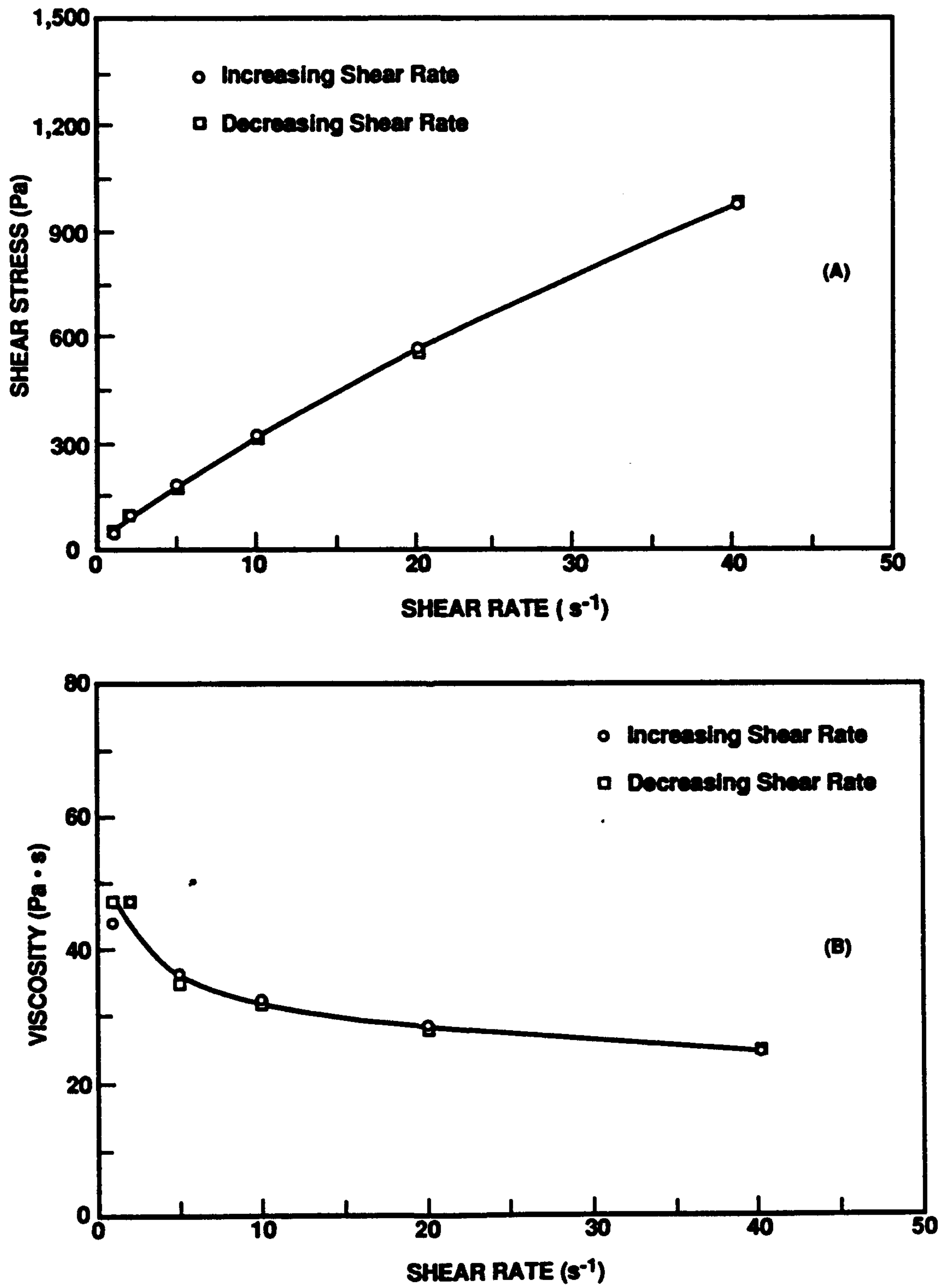
Optimum ratio - excellent spinnability, relatively smooth fiber surfaces

"Spinning Aids" (e.g., PIB, PVS, etc.)

Modify solution rheological characteristics

Modify "green" fiber properties

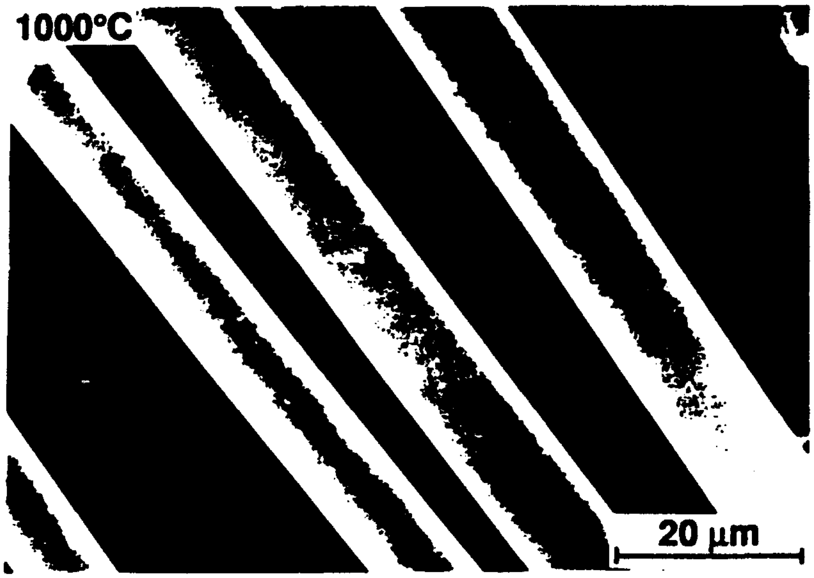

UF Fibers
20°C/min Argon
WEIGHT (%)
100
96
92
88
84
80
76
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE (°C)


1,500
1,200
900
600
300
0
SHEAR STRESS (Pa)
o Increasing Shear Rate
□ Decreasing Shear Rate
(A)
0
10
20
30
40
50
SHEAR RATE (s-1)
80
60
40
20
0
VISCOSITY (Pa • s)
o Increasing Shear Rate
□ Decreasing Shear Rate
(B)
0
10
20
30
40
50
SHEAR RATE (s-1)

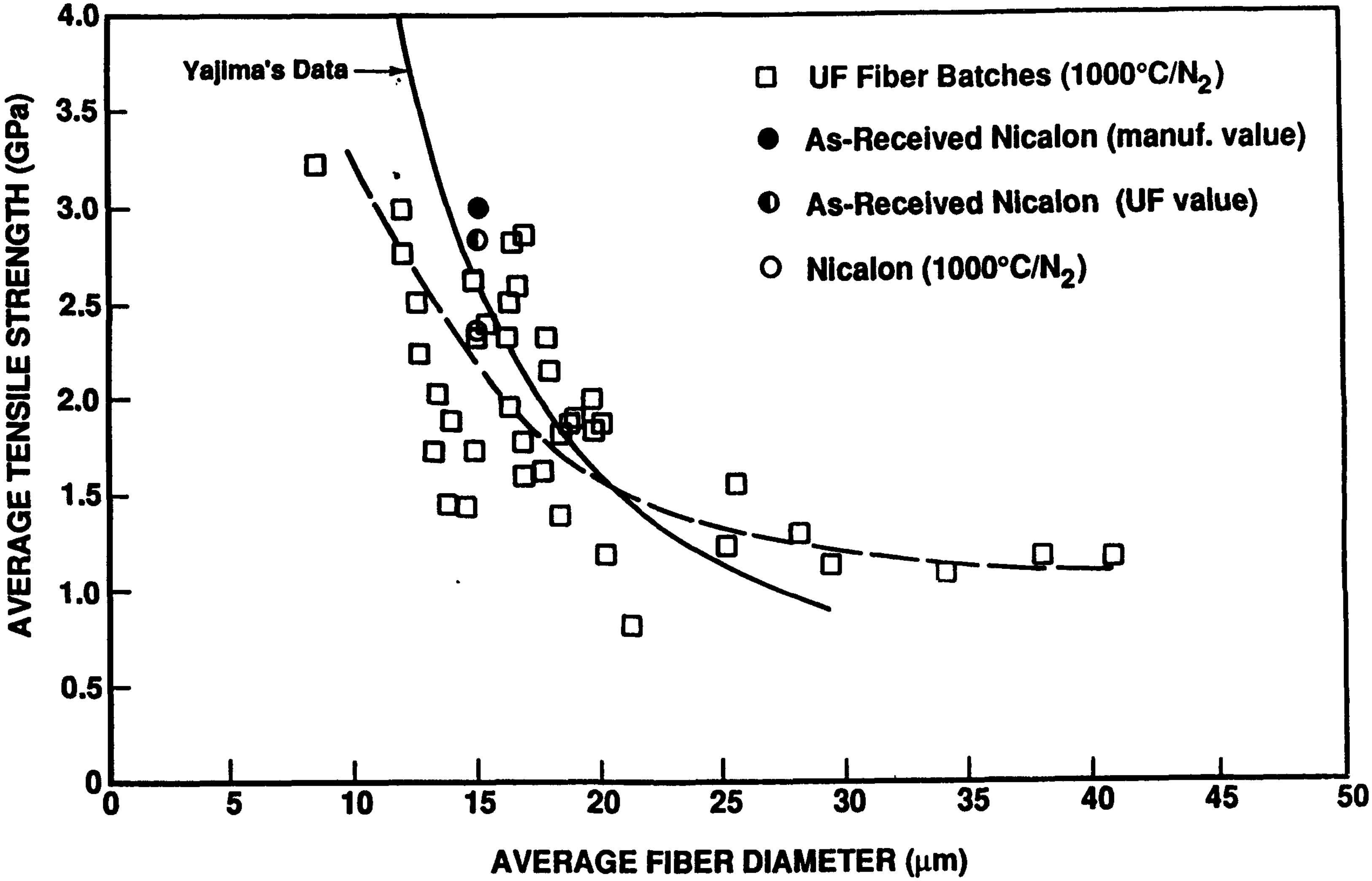
MECHANICAL PROPERTIES OF GREEN AND PARTIALLY-PYROLYZED FIBERS

	Tensile Strength (MPa)	Rupture Strain (%)
UF Fibers Green (as-spun)	20	1.0
UF Fibers (400°C)	44-52	3.5-7.6
Nicalon-type Fibers* (400°C)	~50	~4

* Y. Hasegawa, M. Iimura, and S. Yajima, J. Mater. Sci., 15 720-728 (1980)


1000°C
20 μm

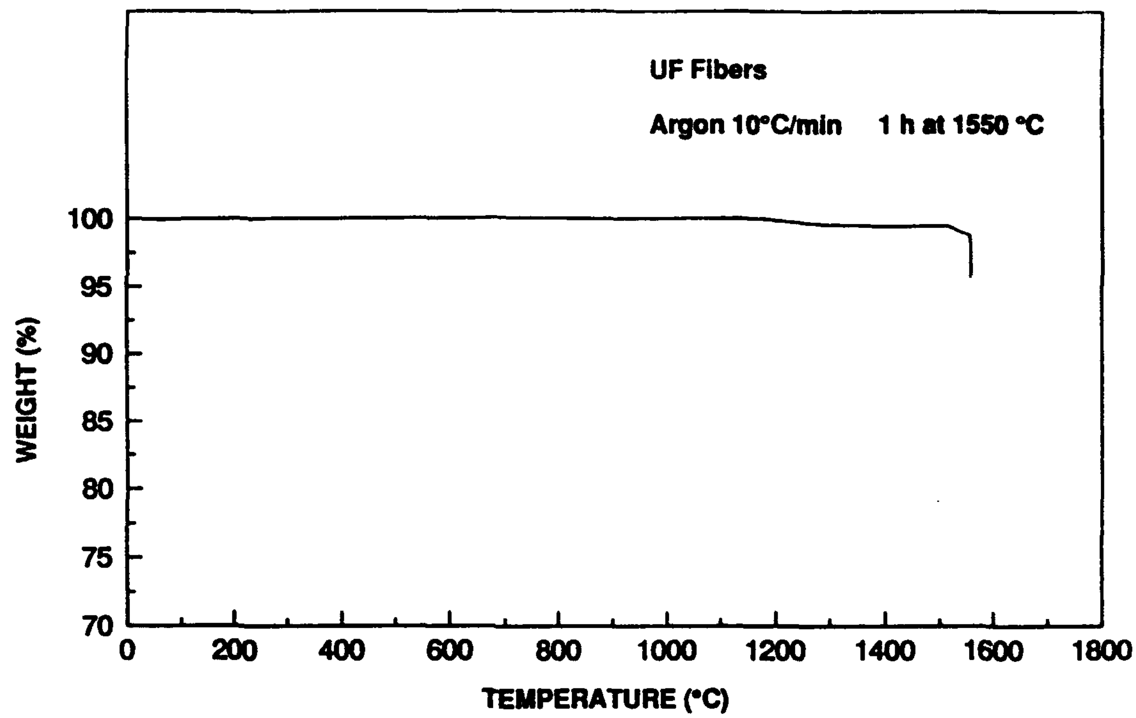

3 μm

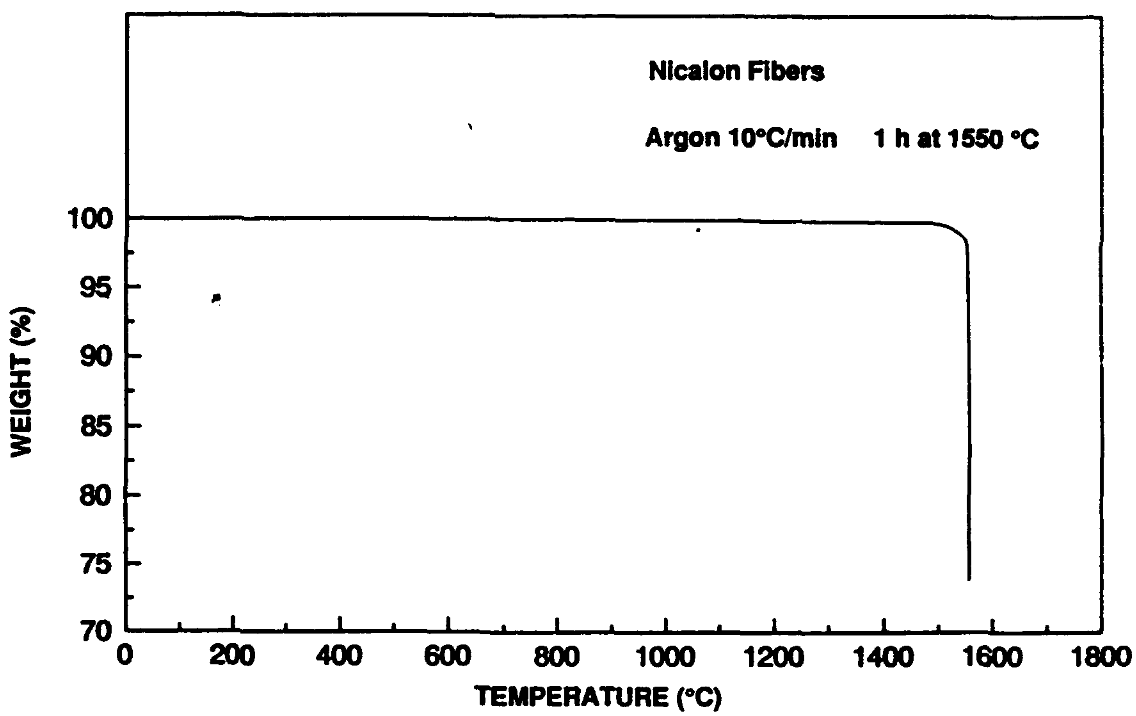

Yajima's Data
UF Fiber Batches (1000°C/N$_2$)
As-Received Nicalon (manuf. value)
As-Received Nicalon (UF value)
Nicalon (1000°C/N$_2$)
AVERAGE TENSILE STRENGTH (GPa)
AVERAGE FIBER DIAMETER (μm)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
5
10
15
20
25
30
35
40
45
50

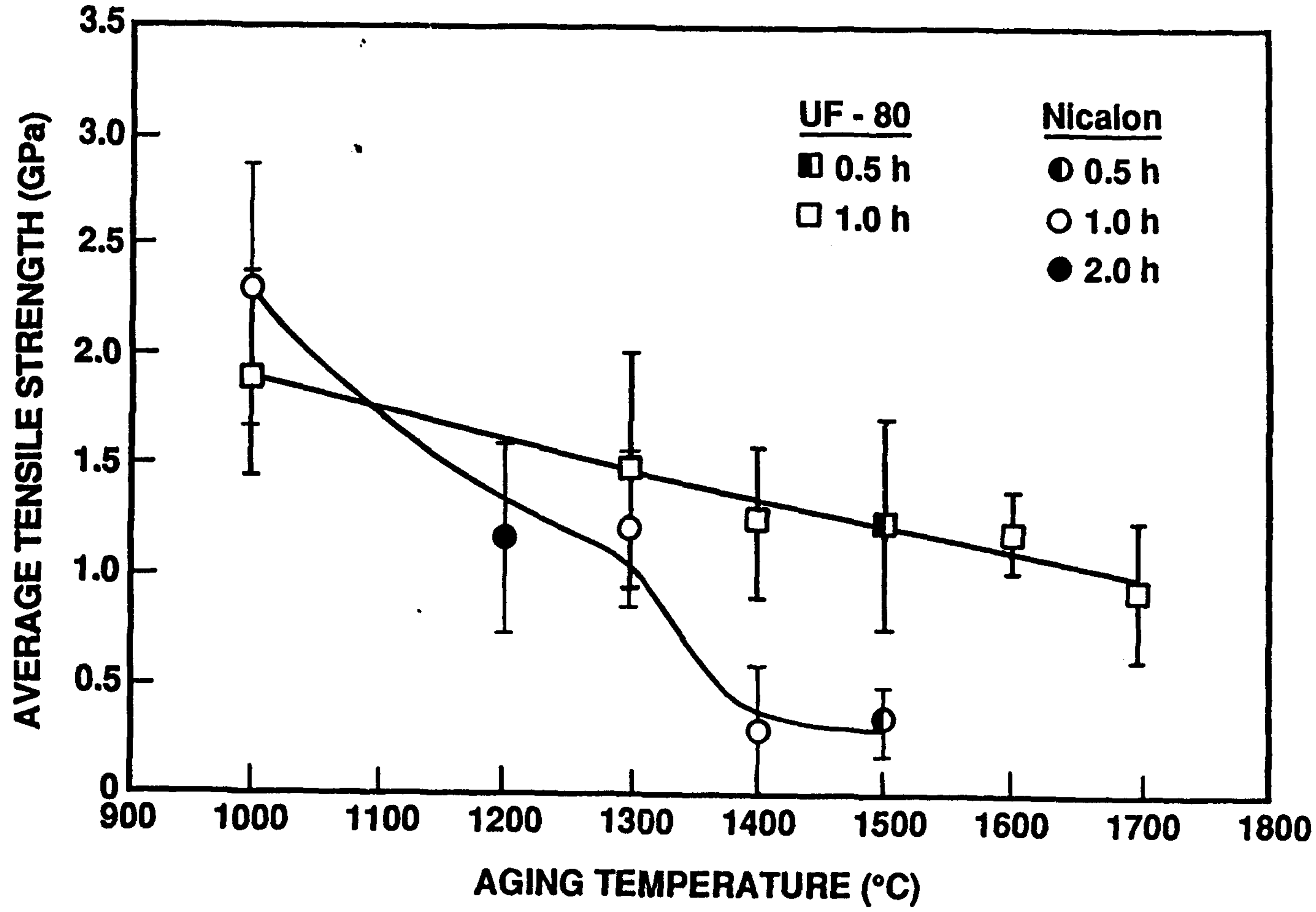
ELEMENTAL ANALYSIS

Sample	O (wt%)	Si (wt%)	C (wt%)	N (wt%)	H (wt%)
UF Fiber	1.1-2.6[†]	55[†,‡]	42[▼]	1-2[▲,†]	<0.5[▲]
Nicalon	13.5-15[†]	55[‡]	29[▲]	<0.5[▲]	<0.5[▲]
Nicalon*	10	58	31		

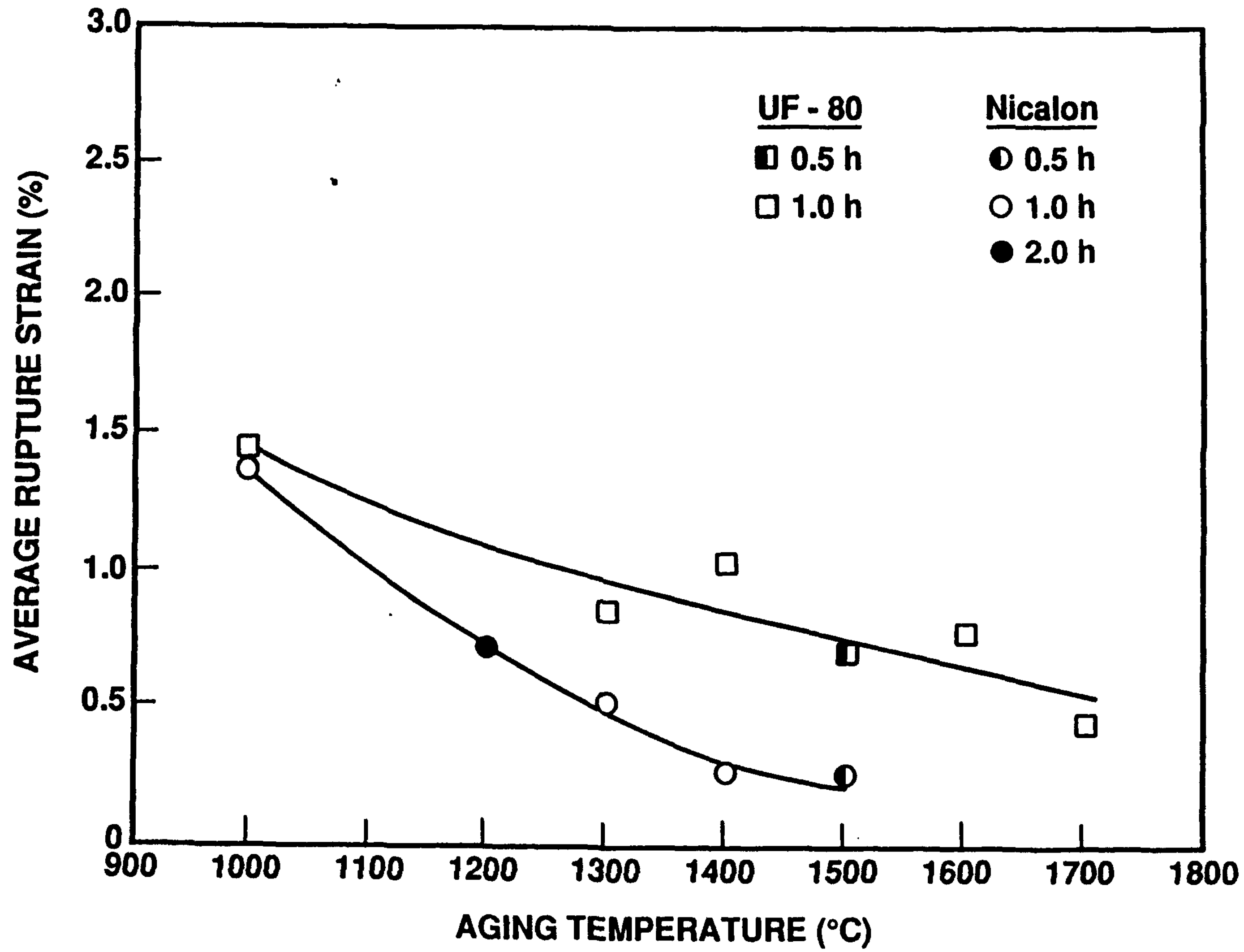
* Reported by manufacturer
† Determined by neutron activation analysis
‡ Determined by atomic absorption
▲ Determined by LECO combustion method
▼ Determined by difference


UF Fibers
Argon 10°C/min 1 h at 1550 °C
WEIGHT (%)
100
95
90
85
80
75
70
0
200
400
600
800
1000
1200
1400
1600
1800
TEMPERATURE (°C)


Nicalon Fibers
Argon 10°C/min 1 h at 1550 °C
WEIGHT (%)
100
95
90
85
80
75
70
0
200
400
600
800
1000
1200
1400
1600
1800
TEMPERATURE (°C)



UF - 80
0.5 h
1.0 h
Nicalon
0.5 h
1.0 h
2.0 h
AVERAGE TENSILE STRENGTH (GPa)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
AGING TEMPERATURE (°C)


AVERAGE RUPTURE STRAIN (%)
3.0
2.5
2.0
1.5
1.0
0.5
0
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
AGING TEMPERATURE (°C)
UF - 80
0.5 h
1.0 h
Nicalon
0.5 h
1.0 h
2.0 h

Processing Modifications

- **Improve Filtration of Spinning Solution**
  (2-4 μm glass filter $\Rightarrow$ 0.1-0.2 μm PTFE filter)

- **Reduce Oxygen Content in Fibers**
  (Lower oxygen partial pressure during pyrolysis)

OXYGEN ANALYSIS*

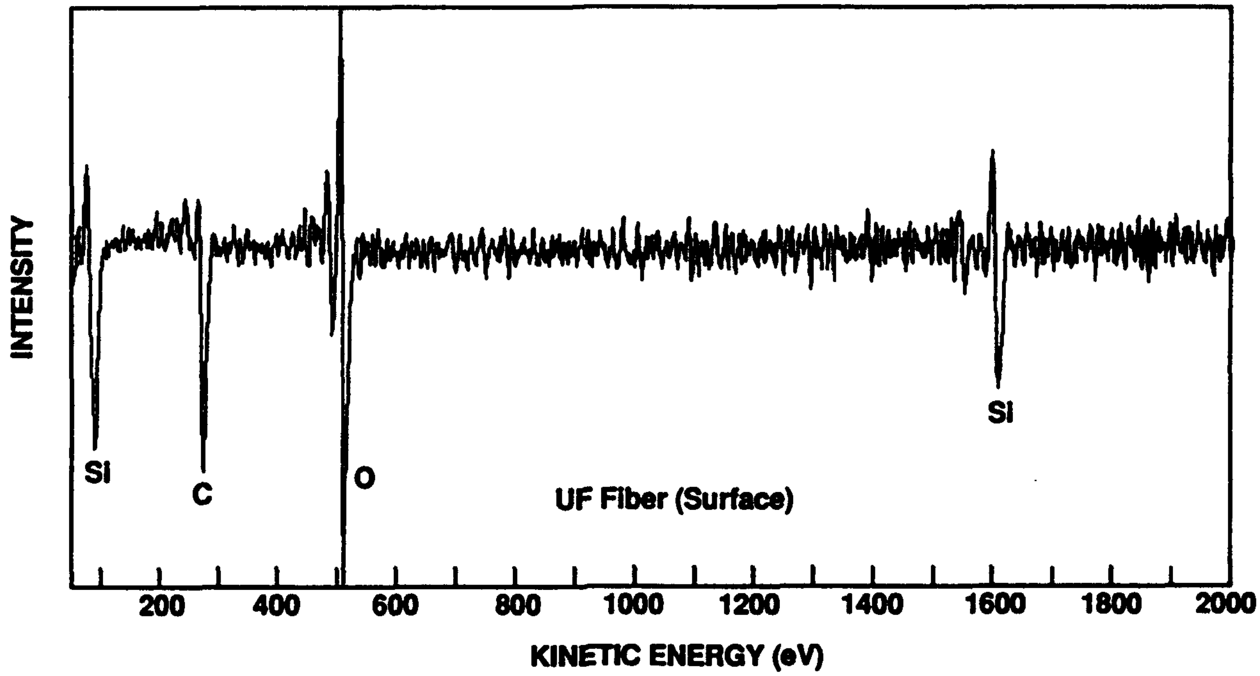
Sample	Weight %
Polydimethylsilane	0.3 - 0.4
Polycarbosilane	0.3 - 1.3
UF FIBER	1.1 - 2.6

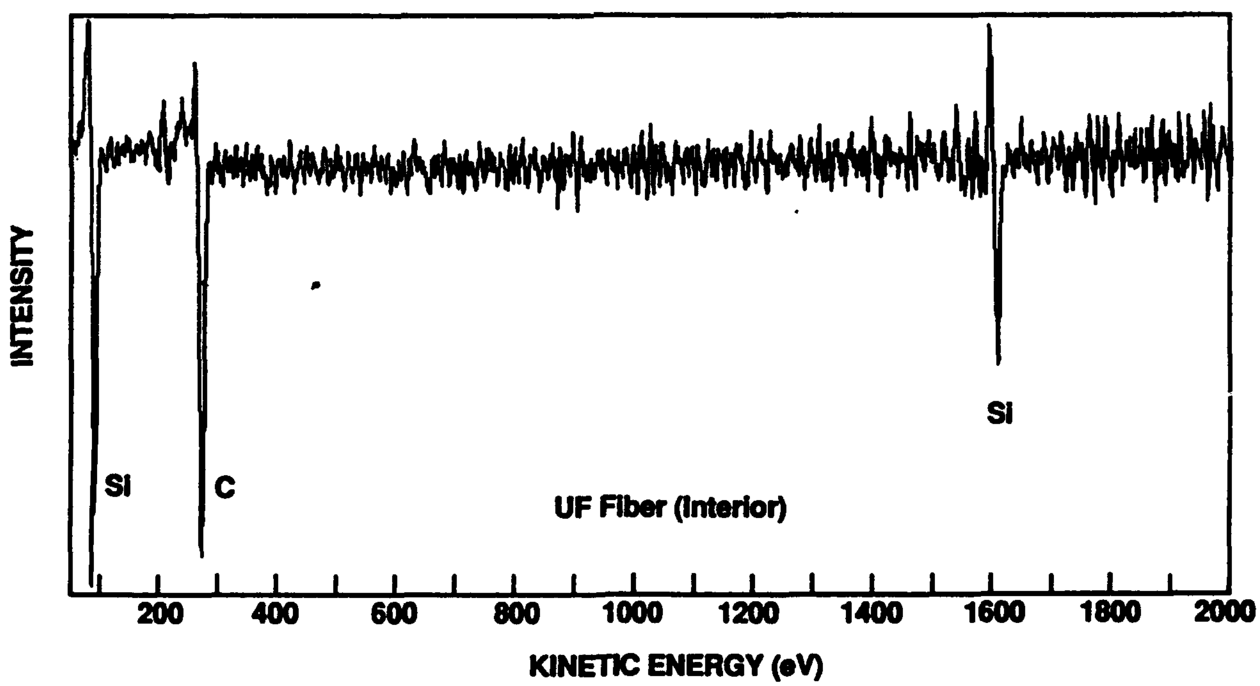
* Determined by neutron activation analysis

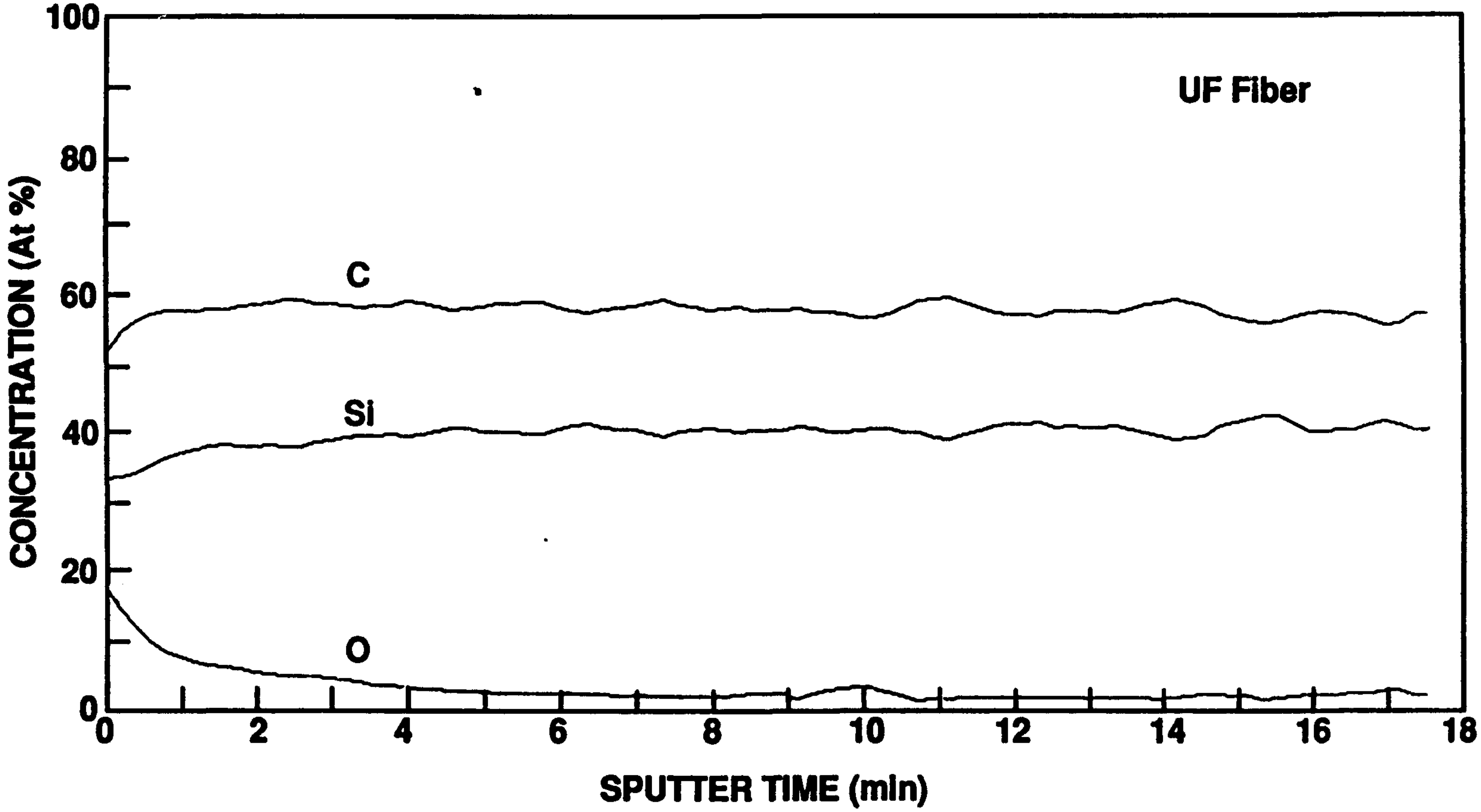
Oxygen Contamination During Fiber Fabrication

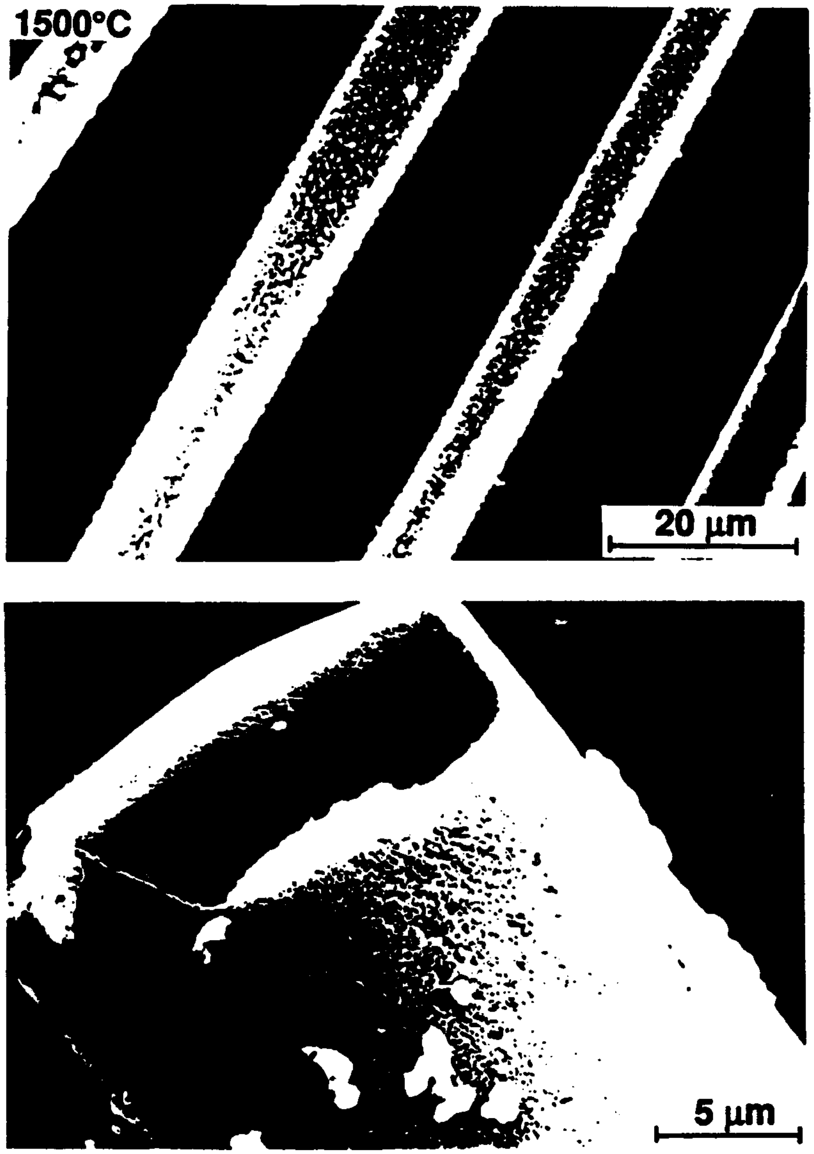
- **Spinning (ambient air atmosphere)**

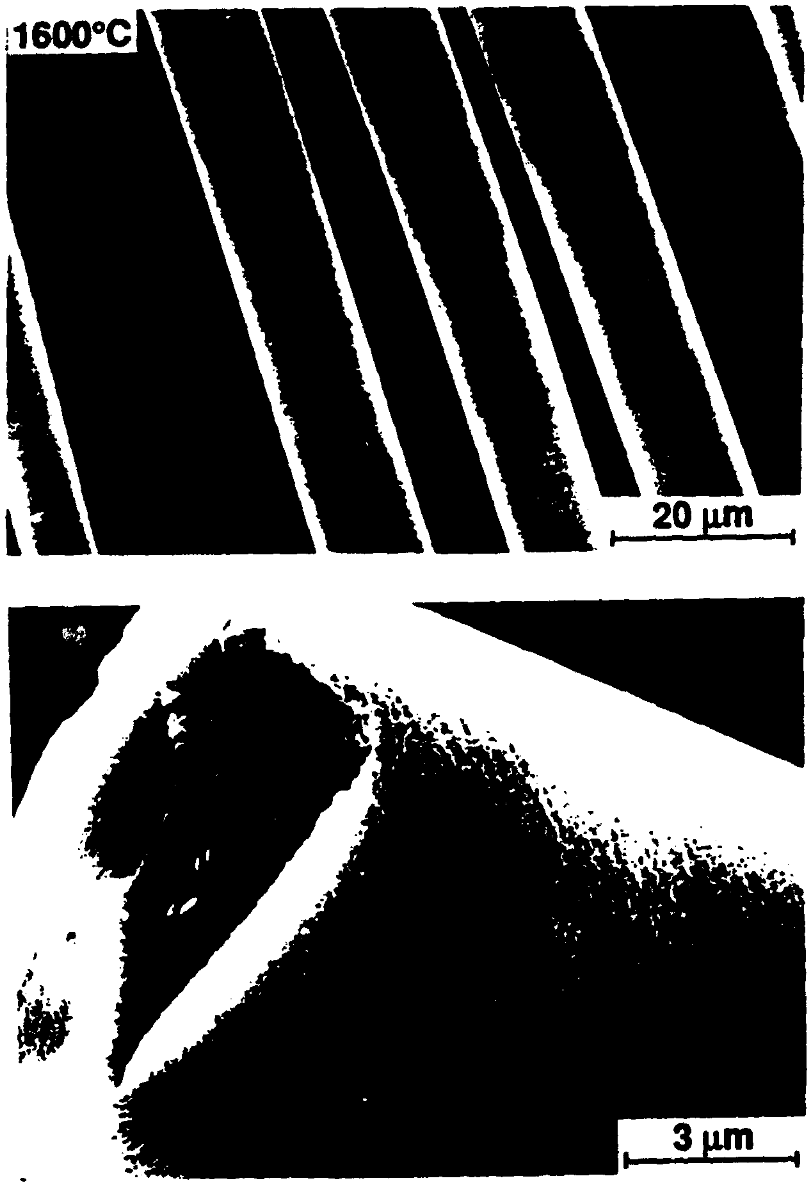
- **Pyrolysis (ungettered furnace, nitrogen)**


INTENSITY
Si
C
O
UF Fiber (Surface)
Si
200
400
600
800
1000
1200
1400
1600
1800
2000
KINETIC ENERGY (eV)

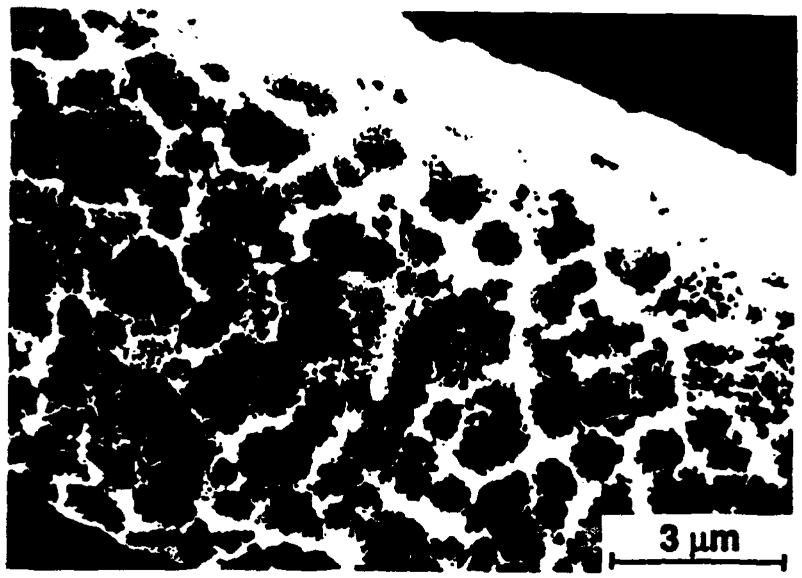

INTENSITY
Si
C
UF Fiber (Interior)
Si
200
400
600
800
1000
1200
1400
1600
1800
2000
KINETIC ENERGY (eV)

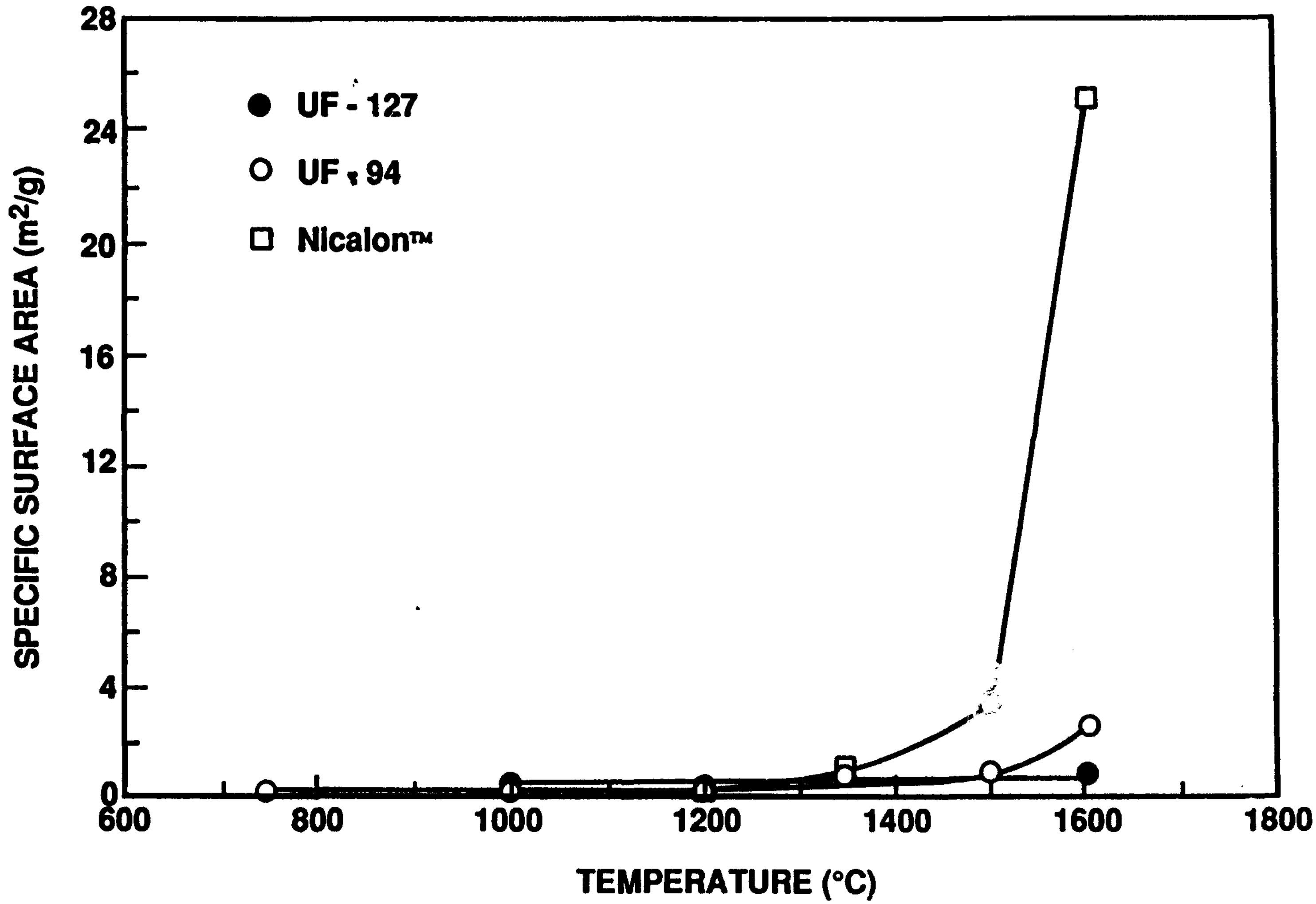

UF Fiber
C
Si
O
CONCENTRATION (At %)
SPUTTER TIME (min)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
18


1500°C
20 µm
5 µm

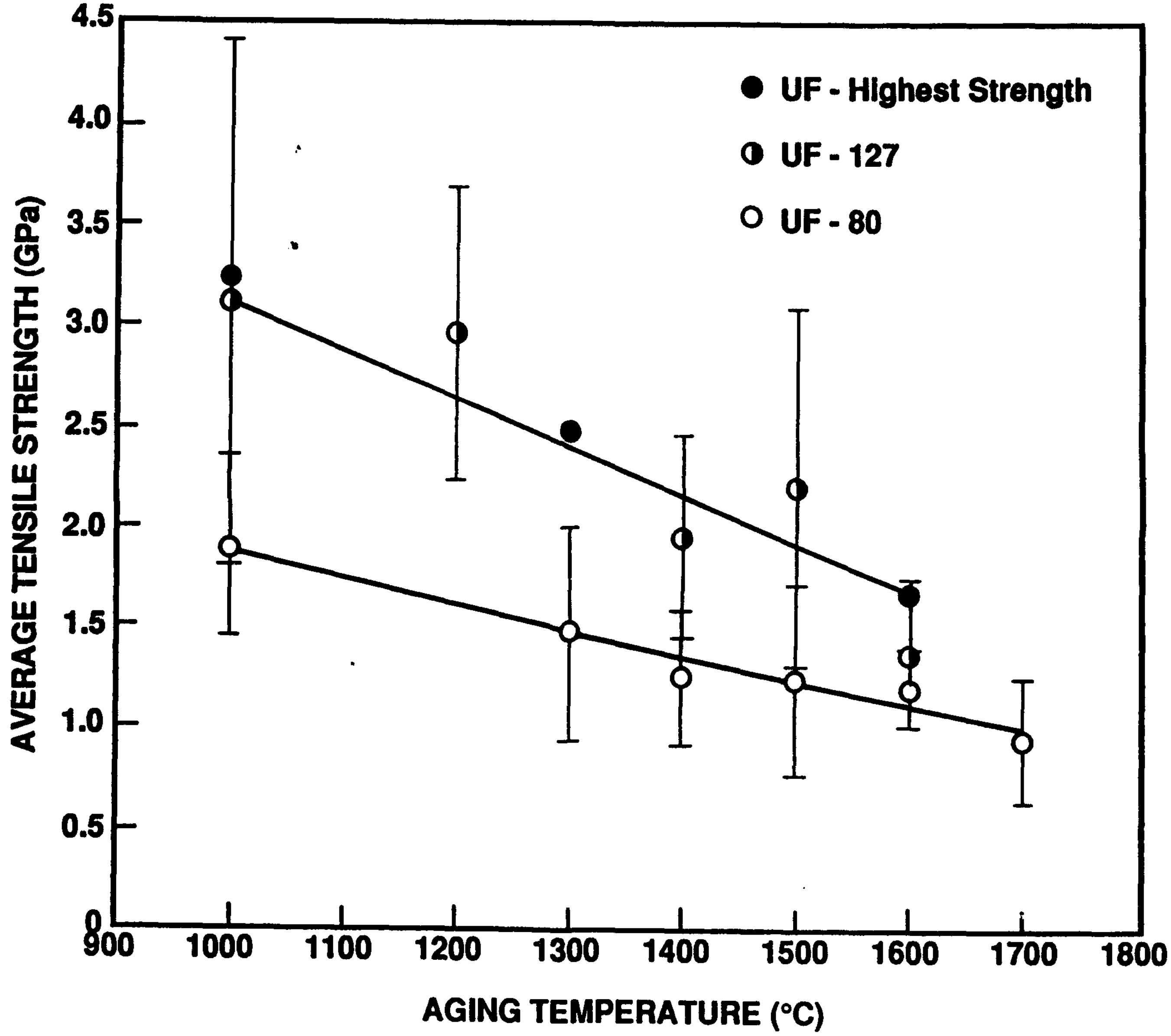

1600°C
20 µm
3 µm

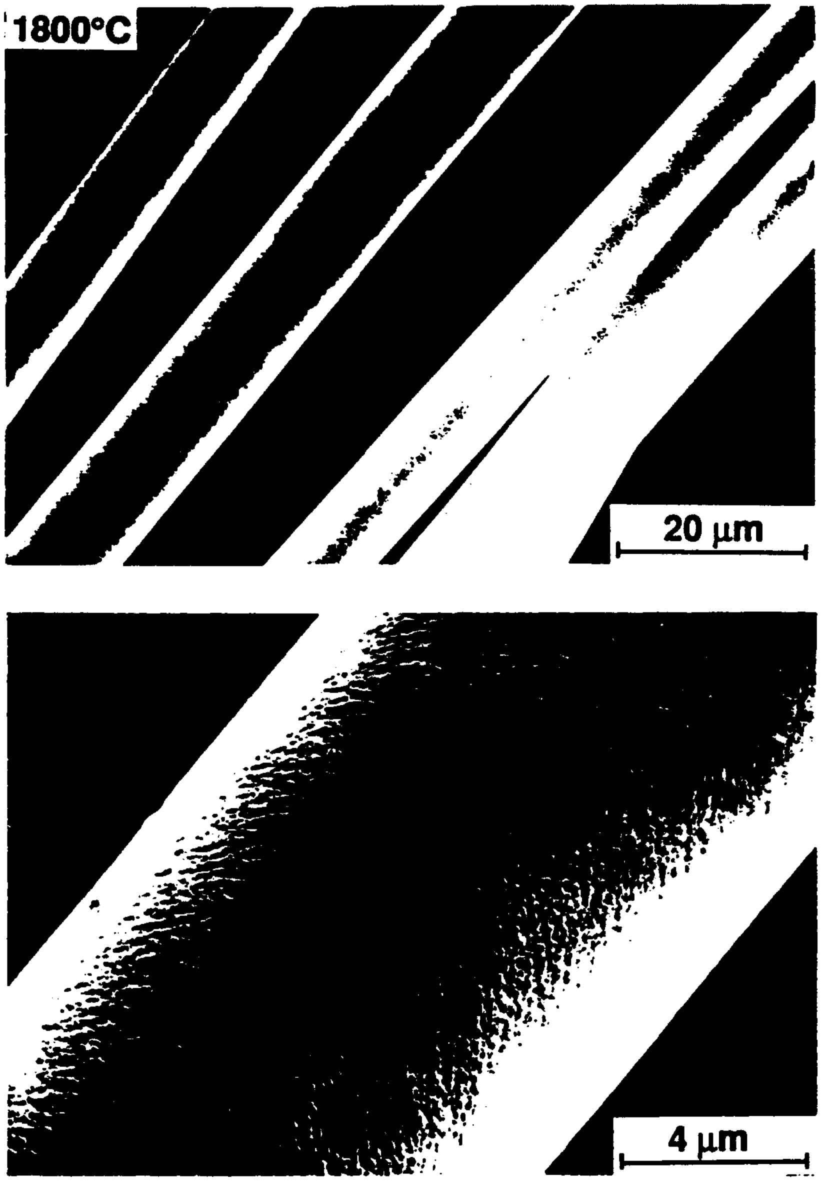
Nicalon™ 1600°C in Argon



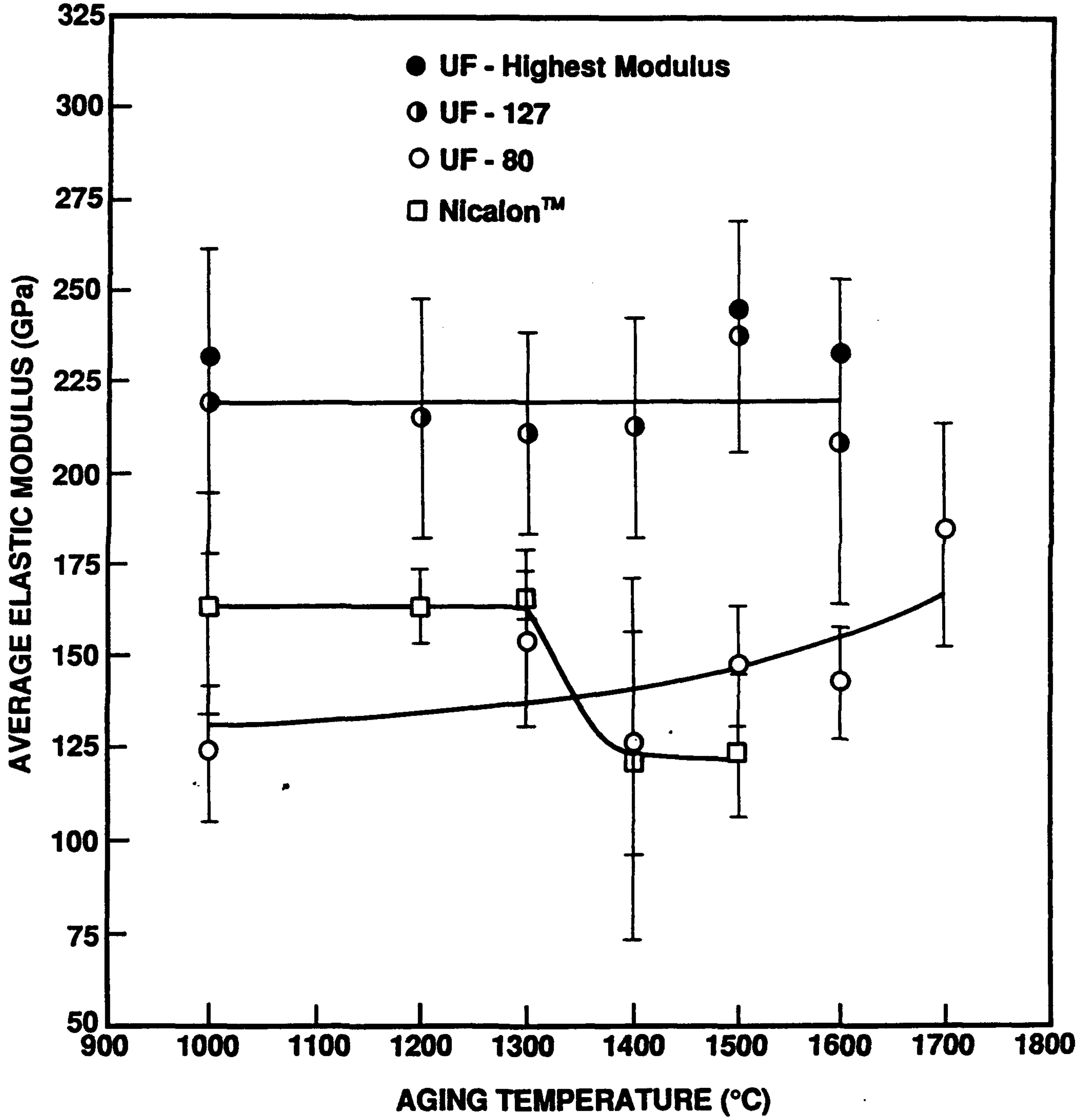


UF - 127
UF - 94
Nicalon™
SPECIFIC SURFACE AREA (m²/g)
28
24
20
16
12
8
4
0
600
800
1000
1200
1400
1600
1800
TEMPERATURE (°C)

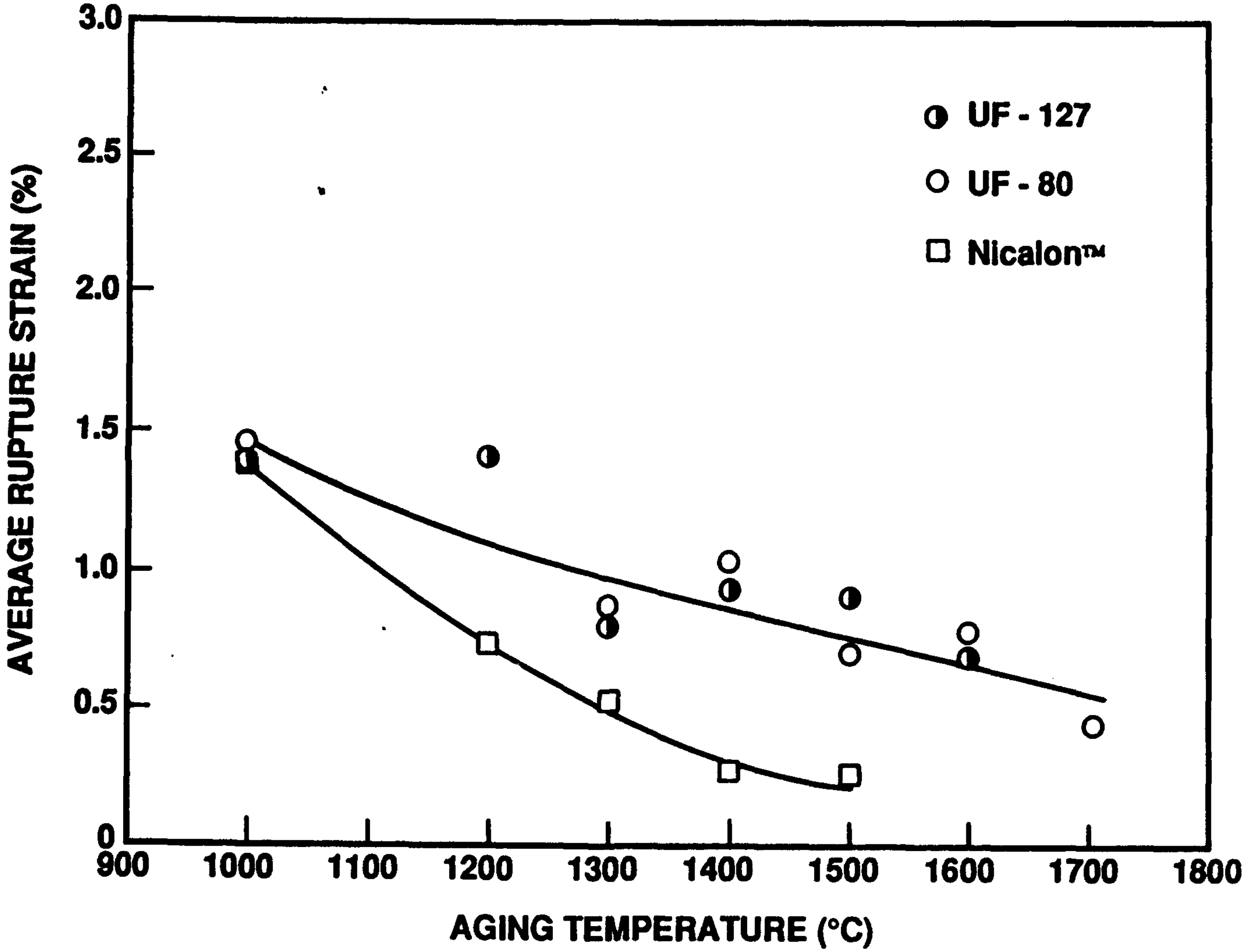

UF - Highest Strength
UF - 127
UF - 80
AVERAGE TENSILE STRENGTH (GPa)
AGING TEMPERATURE (°C)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
900
1000
1100
1200
1300
1400
1500
1600
1700
1800



1800°C
20 μm
4 μm



UF - Highest Modulus
UF - 127
UF - 80
Nicalon™
AVERAGE ELASTIC MODULUS (GPa)
325
300
275
250
225
200
175
150
125
100
75
50
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
AGING TEMPERATURE (°C)



UF - 127
UF - 80
Nicalon™
AVERAGE RUPTURE STRAIN (%)
3.0
2.5
2.0
1.5
1.0
0.5
0
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
AGING TEMPERATURE (°C)

SUMMARY

UF fibers were prepared by dry spinning of concentrated solutions of high molecular weight (~5,000-10,000) polycarbosilane (PC) (with spinning aids) and subsequent pyrolysis of the polymer fibers

Processing

- No oxidative or irradiative cross-linking step
- Polymers solutions have excellent spinnability
- High ceramic yield after pyrolysis
- Green and partially-pyrolyzed fibers have good mechanical properties

Properties

- Fibers with low oxygen content (~1-2%), range of diameters (~8-50 μm), round cross-sections, and relatively smooth surfaces
- Average tensile strengths as high as ~3.3 GPa for as-pyrolyzed fibers
- Average rupture strain ~1.5% for as-pyrolyzed fibers
- Average tensile strength as high as 2.3 GPa and average elastic modulus as high as 250 GPa after 1500°C (1 h) heat treatment in argon
- Average tensile strength as high as 1.9 GPa and average elastic modulus as high as 235 GPa after 1700°C (1 h) heat treatment in argon

FUTURE DIRECTIONS

- **Optimization of Fiber Processing Conditions**
- **Additional Characterization of Fibers**
- **Compositional Modification/Microstructural Development**
- **Scale-Up**

Optimization of Fiber Processing Conditions

Polymer Characteristics
PC molecular weight distribution
Spinning aid characteristics (e.g., molecular weight)
PC/spinning aid ratio
Purity

Spinning Dope Characteristics
Solution rheological characteristics
Polymer/solvent ratio
Solvent type
Purity

Spinning Process
Spinneret geometry
Extrusion pressure
Drying conditions (temperature, atmosphere, gas flow)
Winding conditions

Pyrolysis conditions
Heating schedule
Atmosphere
Continuous vs. batch process
Tensioning

Process Controls/Sensors for Optimization of Fiber Fabrication

Metering pump

De-airing station

In-line filtration station

Viscosity sensor

Spinneret head temperature and pressure sensors

Multistage spinning/drying chamber (temperature/atmosphere controls)

Sensors to monitor temperature, gas composition, gas flow rate, and fiber diameter in spinning/drying chamber

Frictionless winders

Continuous pyrolysis facility

Fiber Characterization

Microstructure and Properties

High temperature testing (e.g., strength, creep) in oxidizing and non-oxidizing atmospheres

Detailed TEM analysis and compositional mapping

Fracture analysis

Suitability for Composite Fabrication

Fiber weavability

Stability under compositing conditions (e.g., high temperature/ high pressure)

Microstructural Development/Compositional Modification

- Lower Oxygen Content
- Increased Si:C ratio
- Oriented Grain Structures

Co-Workers/Contributors

Wm. Toreki
M. Saleem
G.J. Choi
E.J. Serrano
B.J. Madana
A.A. Morrone
E. Lambers

Solution or Melt Spinning?

- Earliest fibers were solution spun:
  natural - silk
  synthetic - cellulose, i.e. rayon

- Current high volume fibers are melt spun:
  glass fiber
  nylon
  PET, i.e., Dacron
  (Nicalon)

Advantages of Melt Spinning

Simple process (no solvent)
High speeds
Complex cross-section (trilobal, etc.)

Disadvantages

Narrow range of operation
Hard to include additives

High Performance Fibers Now Are Solution Spun

Kevlar (DuPont)
Spectra (Allied-Signal)

UF-SiC Fiber Technology Extendable Since

- Very robust (wide range of conditions work)
- Additives easy to incorporate by viscosity changes (even if immiscible)

Extendable (continued)

- Same solutions can be used for coatings (original goal)
- Synthesis modification has potential for infiltration
- Same benefits for BN precursors and others

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

Joseph H. Simmons, Anthony B. Brennan, Michael D. Sacks

Salwan Al-Assafi, Tom Miller and Terry Cruse

Department of Materials Science and Engineering
University of Florida
Gainesville, FL 32611

Help with the Electron Microscopy was provided by:
Augusto Morrone

DARPA

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

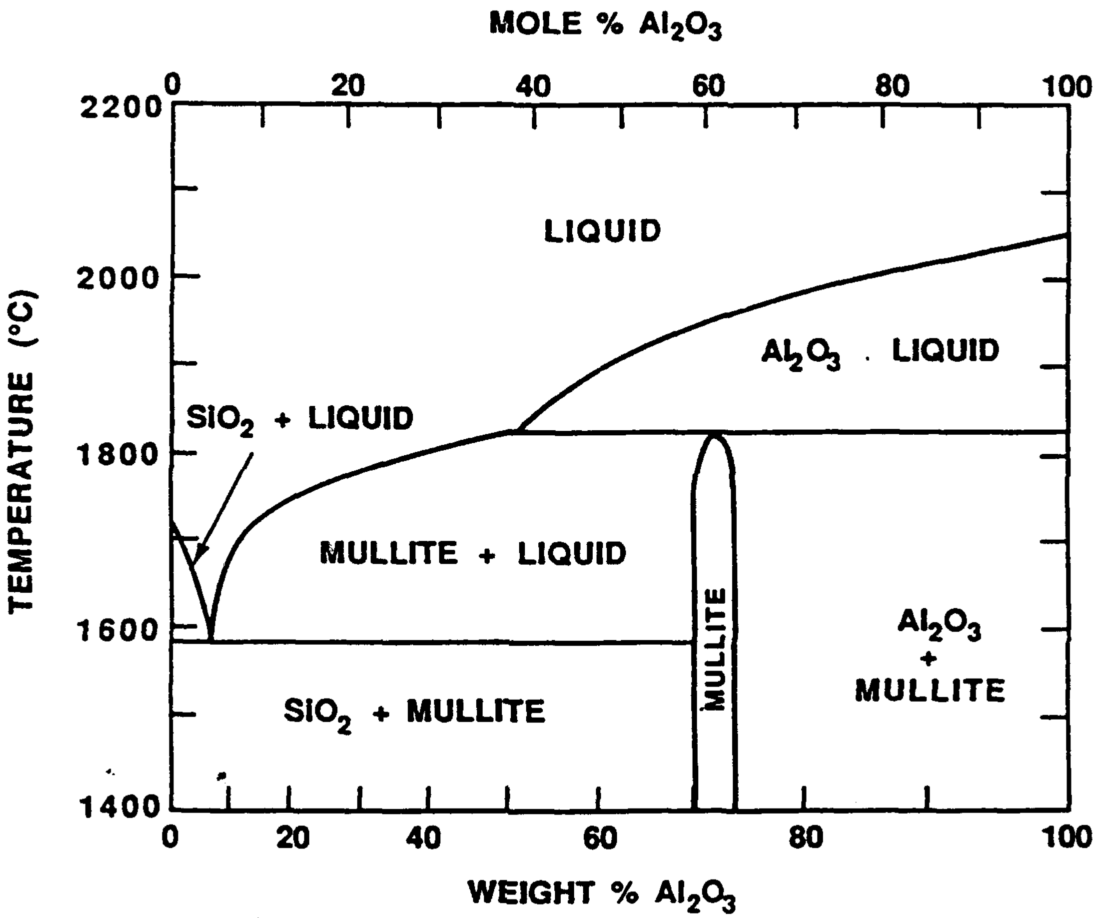
OBJECTIVE

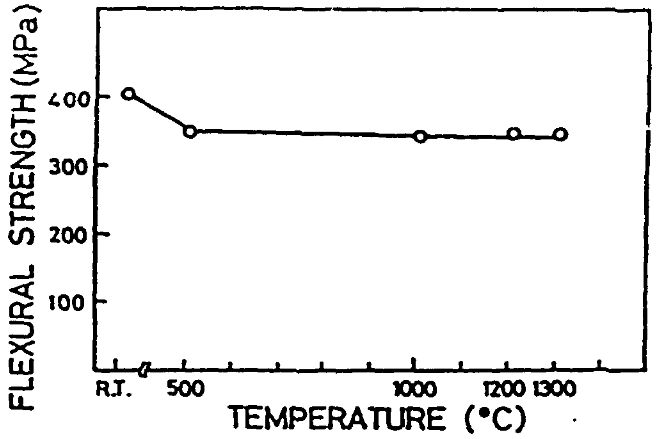
- To develop a solution-based process for the continuous and AI controlled spinning of high-strength mullite and composite mullite fibers with improved high temperature (>1200C) properties.

APPROACH

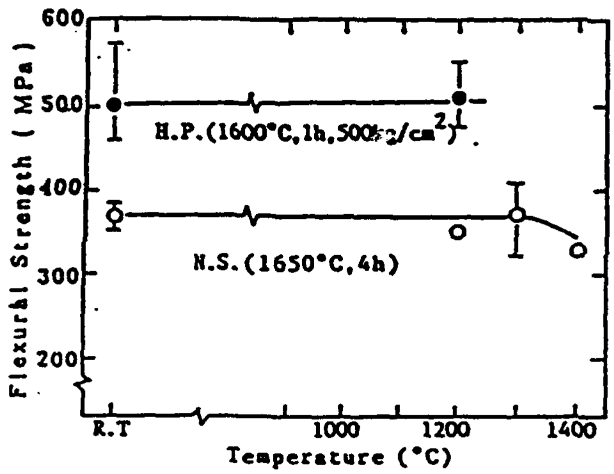
- Use a precursor sol approach to produce fine-grained mullite and mullite matrix composites with no intergranular glass phase.
- Develop a relationship between precursor sol chemistry and fiber spinning / ceramic processing characteristics in order to pre-determine and control sintered fiber properties, composition and phase structure.
- Relate processing conditions and microstructure to high temperature mechanical characteristics.
- Develop AI-based fiber spinning and processing operations.

SiO_2 - Al_2O_3 PHASE DIAGRAM

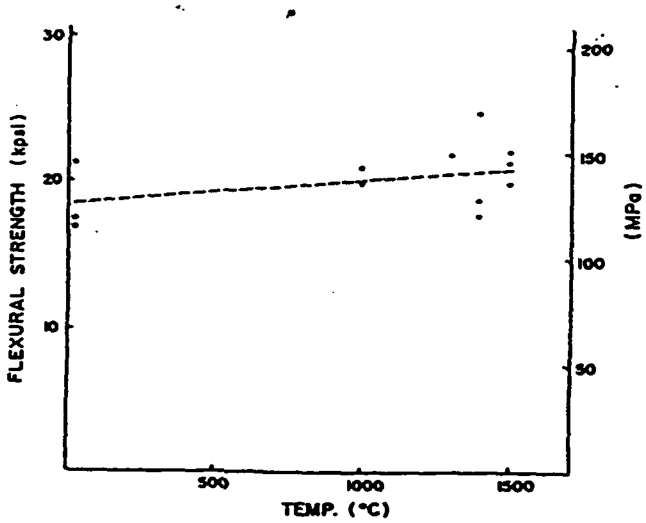




M.G.M.U. Ismail, Z. Nakai, and S. Sōmiya, J. Am. Ceram. Soc., 70(1) C-7 - C-8 (1987)



S. Kanzaki and H. Tabata, pp 51-61 in "Mullite" edited by S. Sōmiya, Uchida Rokakuho Publishing Co., Tokyo, Japan, 1985



T. Mah and K.S. Mazdiyasni, J. Am. Ceram Soc., 66 (10) 699-703 (1983)

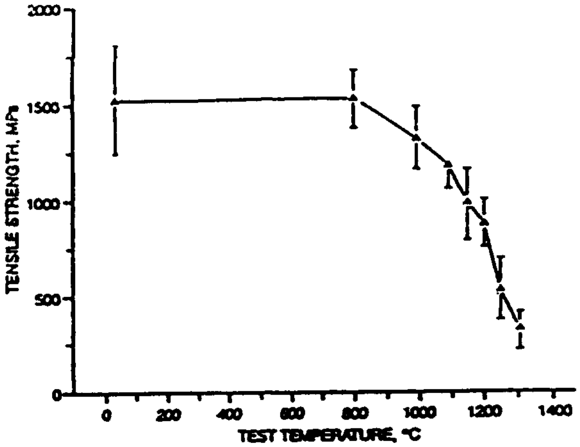


Fig. 7. Hot tensile strength of Nextel 480 filaments measured at various temperatures in air.

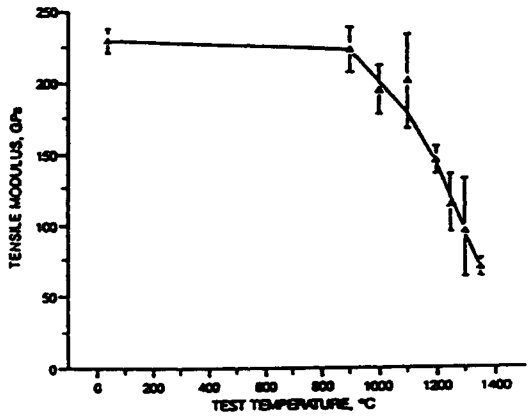


Fig. 8. Hot elastic modulus of single filaments of Nextel 480 measured at various temperatures in air.

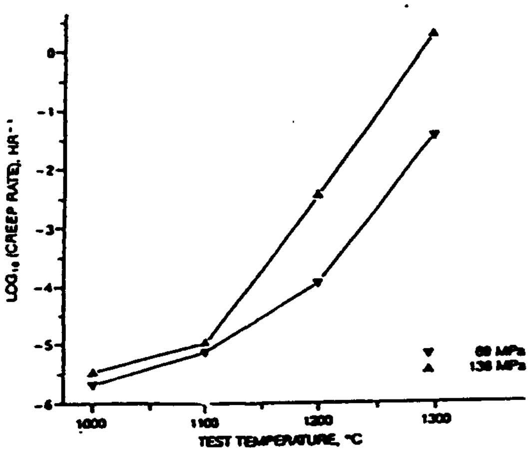


Fig. 9. Creep rate of Nextel 480 roving measured at various temperatures in air.

D.D. Johnson, A.R. Holtz, and M.F. Grether, Ceram. Eng. Sci. Proc., 8(7-8) 744-754 (1987)

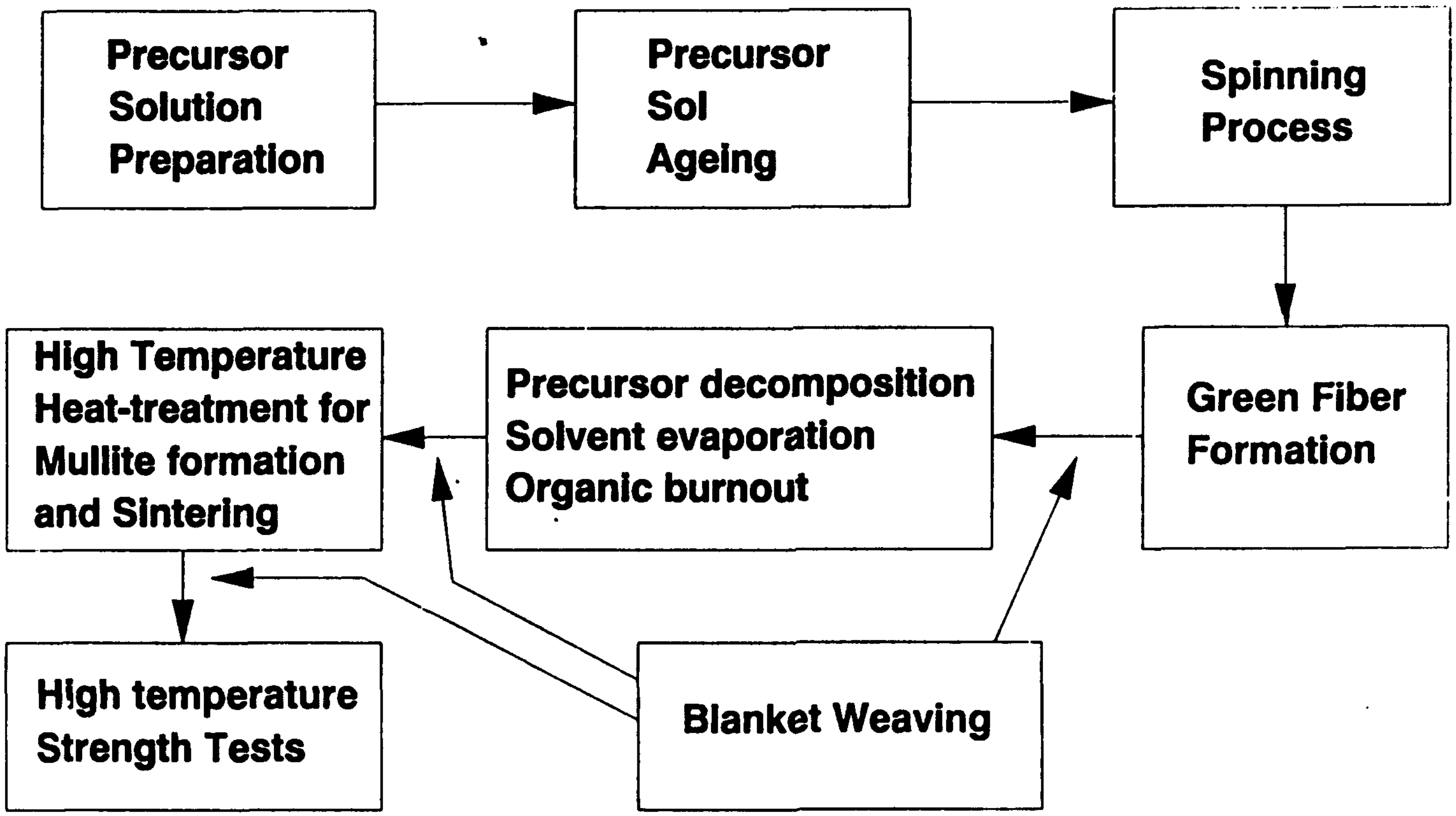
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

STATEMENT OF PROBLEM

- Degradation in mechanical behavior of composite fibers limits applications to temperatures below 1200°C.
- Non-oxide composition of most high temperature fibers limits their ability to withstand high temperature exposure to oxygen-containing atmospheres.
- Possible causes for mechanical degradation of composite fibers at high temperatures:
  - Residual glass phase at grain boundaries
  - Chemical reactions with ambient atmosphere or matrix material
  - Microstructure instabilities (e.g. grain growth) at high temperatures
  - Activation of slip (dislocation motion or generation) and/or diffusional creep
  - Incomplete densification (Modelling studies show that voids act as stress concentrators and nucleation sites for cracks)

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

TYPICAL PROCESS



SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

ADVANTAGES OF PROCESSING WITH SOL PRECURSORS

- Access to a wide range of precusor compositions and structures
  - Control over intermediate phases and final phase structure
  - Potential avoidance of intergranular glass phase

- Potential for independent control over sintering and crystal phase formation
  - Full density without sintering aids
  - Control of grain growth

- Low temperature fiber spinning and better AI controls

- High temperature sintering after handling can heal surface flaws from handling-spinning-weaving

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

CRITICAL PROBLEMS IN CONTINUOUS FIBER SPINNING FROM SOL-GEL PRECURSORS

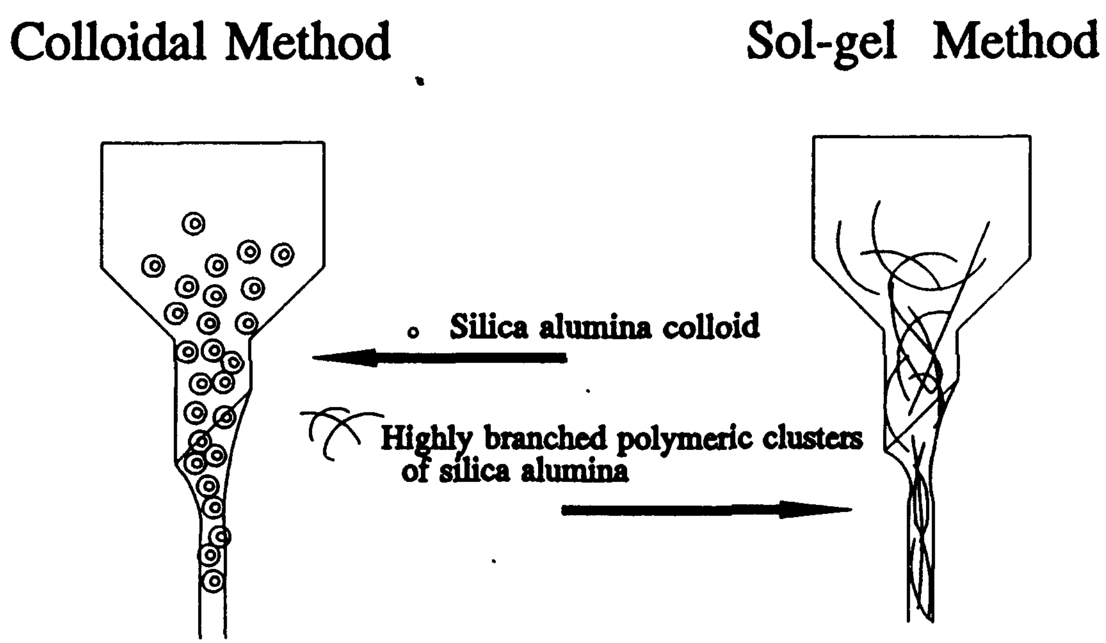
- Selection of solution precursors: colloidal vs polymer vs seeding
  - Component compatibility (prehydrolysis, sol stabilization, etc.)
  - Timing of hydrolysis/condensation reactions for each component

- Development of desirable rheological behavior in the precursor sol
  - Sol must be stable at low viscosity in the holding tank
  - Sol must quickly reach spinning viscosity at the spineret
  - Spun fiber must solidify rapidly after extrusion past the spineret

- Green fiber characteristics
  - Green fiber must be flexible and strong in order to withstand spooling on take-up drum
  - Fiber surface must resist handling and spooling damage in green condition

- Drying and sintering
  - Pronounced shrinkage during heating
  - Polymer burnout and carbonaceous residues
  - Phase transformations vs viscous phase sintering / no residual glass phase
  - Continued handling damage

Comparison of Fiber Processing Methods



Method #1: Centrifugal Spinning
Method #2: Pulled by Hand

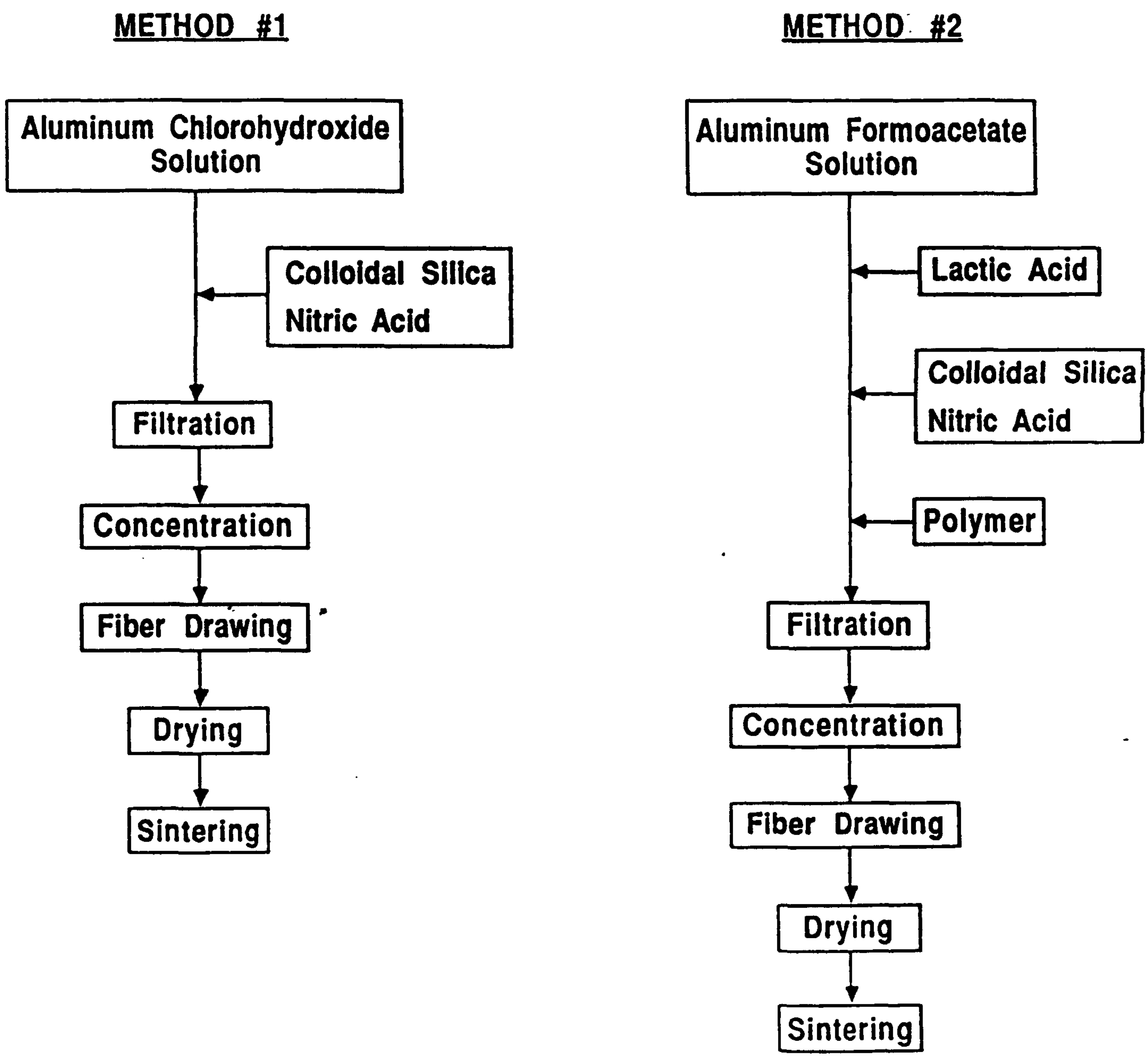
Continuous Spinning

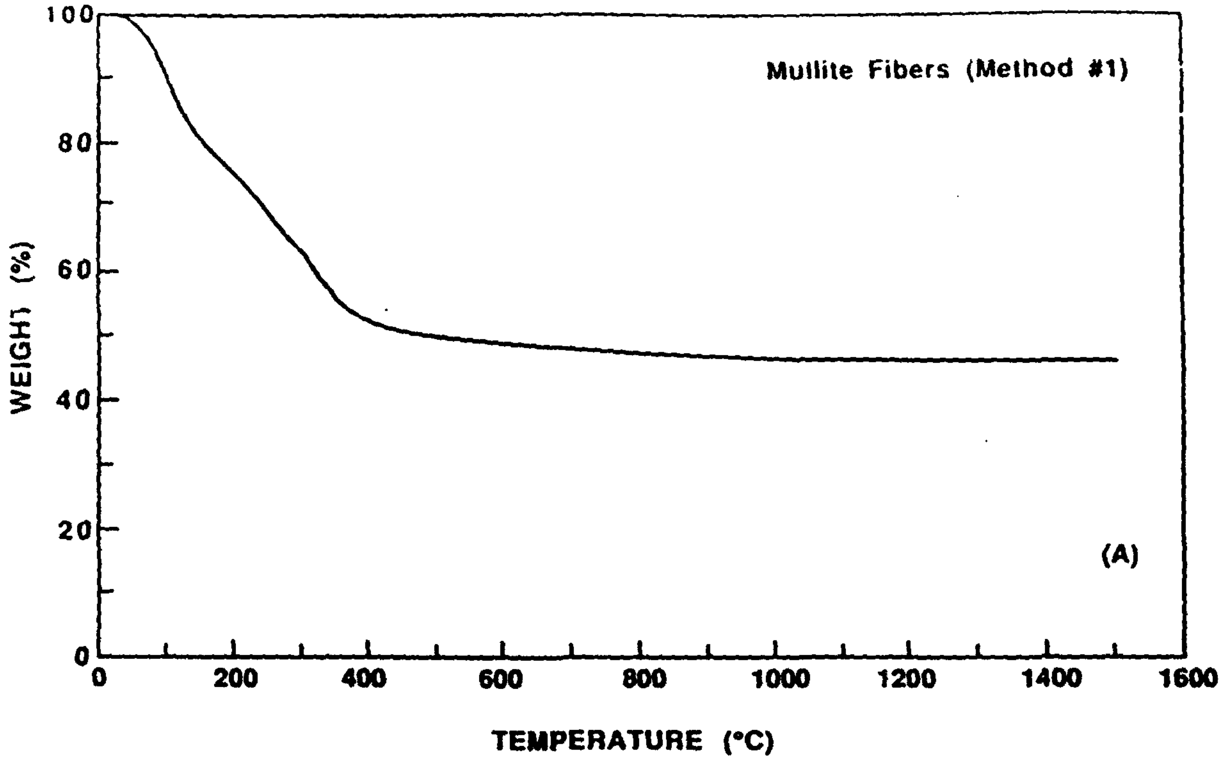
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

DETAILED APPROACH

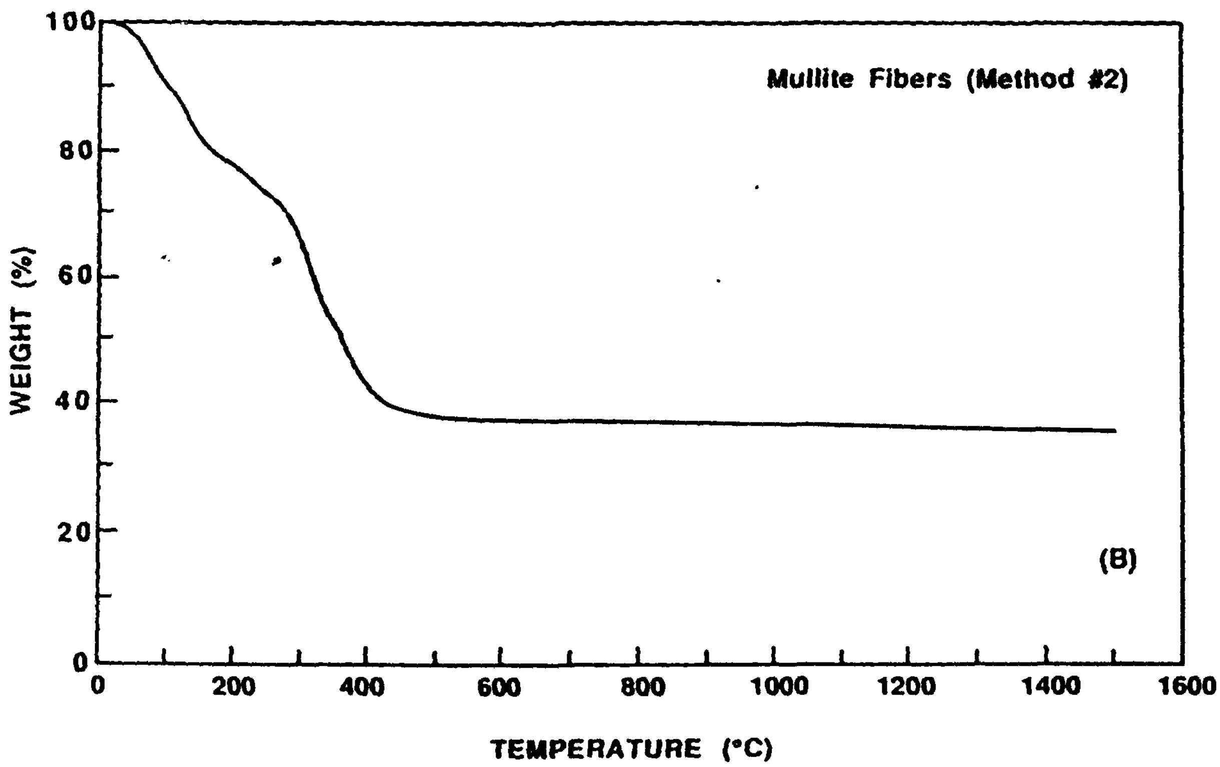
- Precursor sol chemistry variations:
  - alkoxide precursors (polymeric) vs colloidal precursors vs seeding
  - effect of solution stabilization aids
  - effect of fiber spinning aids
- Process variations:
  - treatment of fiber at spinning nozzle
  - precusor decomposition and organic burnout
  - mullite transition reaction and effect of intermediate phases
  - sintering kinetics and grain size control

MULLITE FIBER FABRICATION

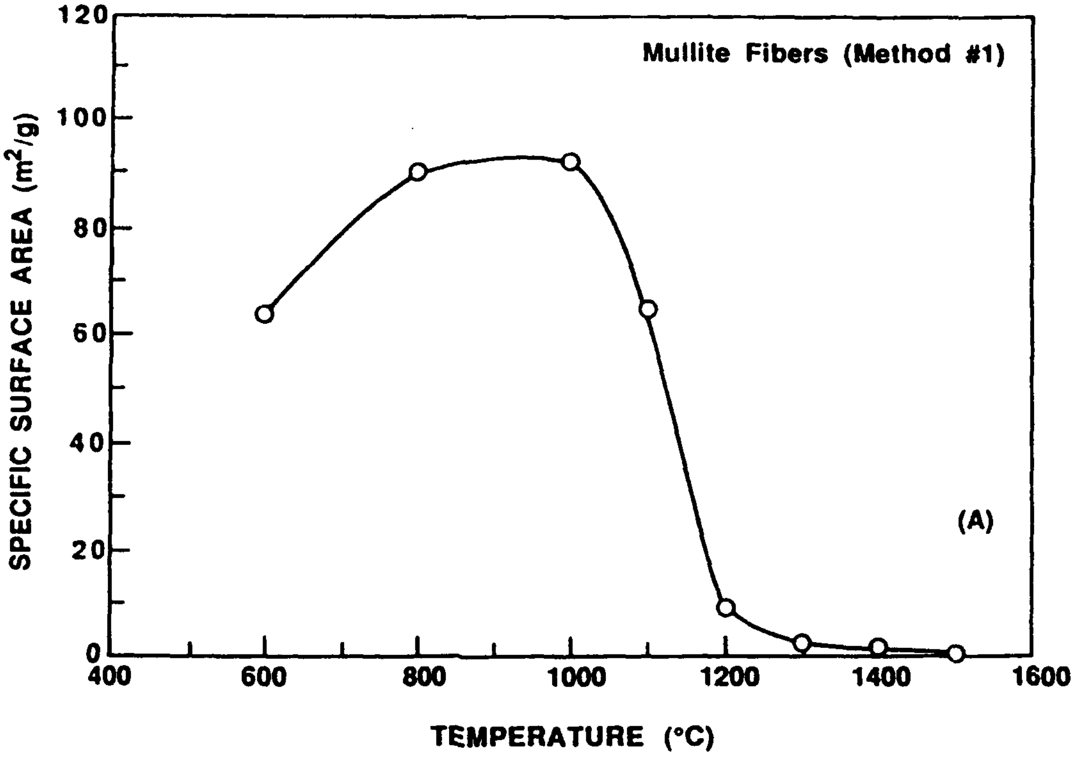


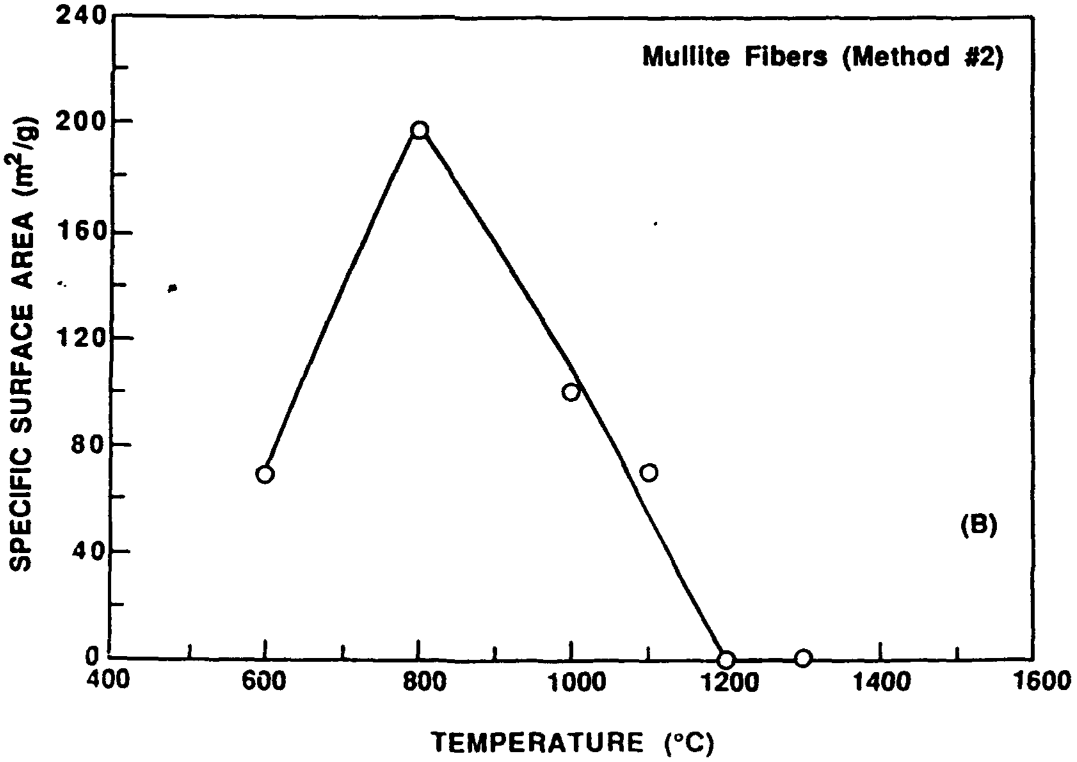


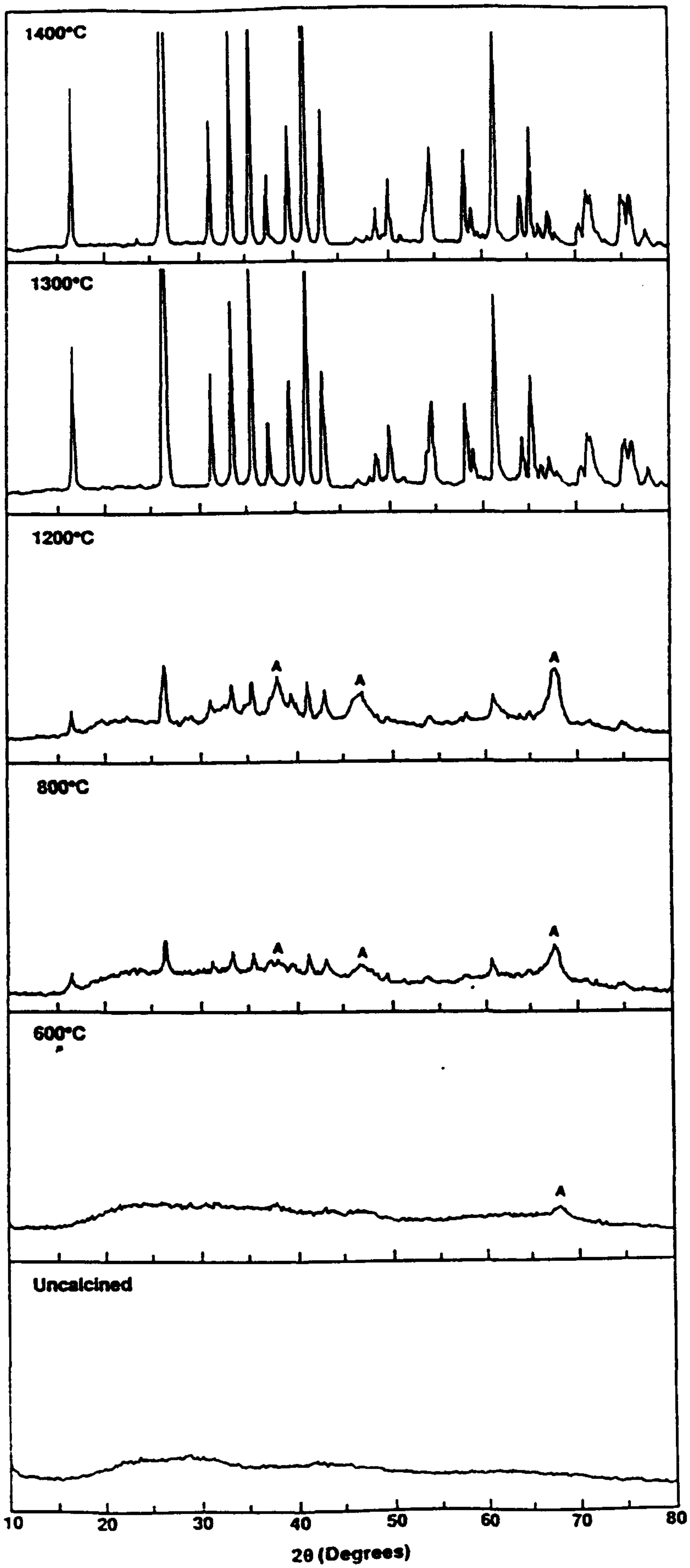
Mullite Fibers (Method #1)
(A)
WEIGHT (%)
100
80
60
40
20
0
0
200
400
600
800
1000
1200
1400
1600
TEMPERATURE (°C)



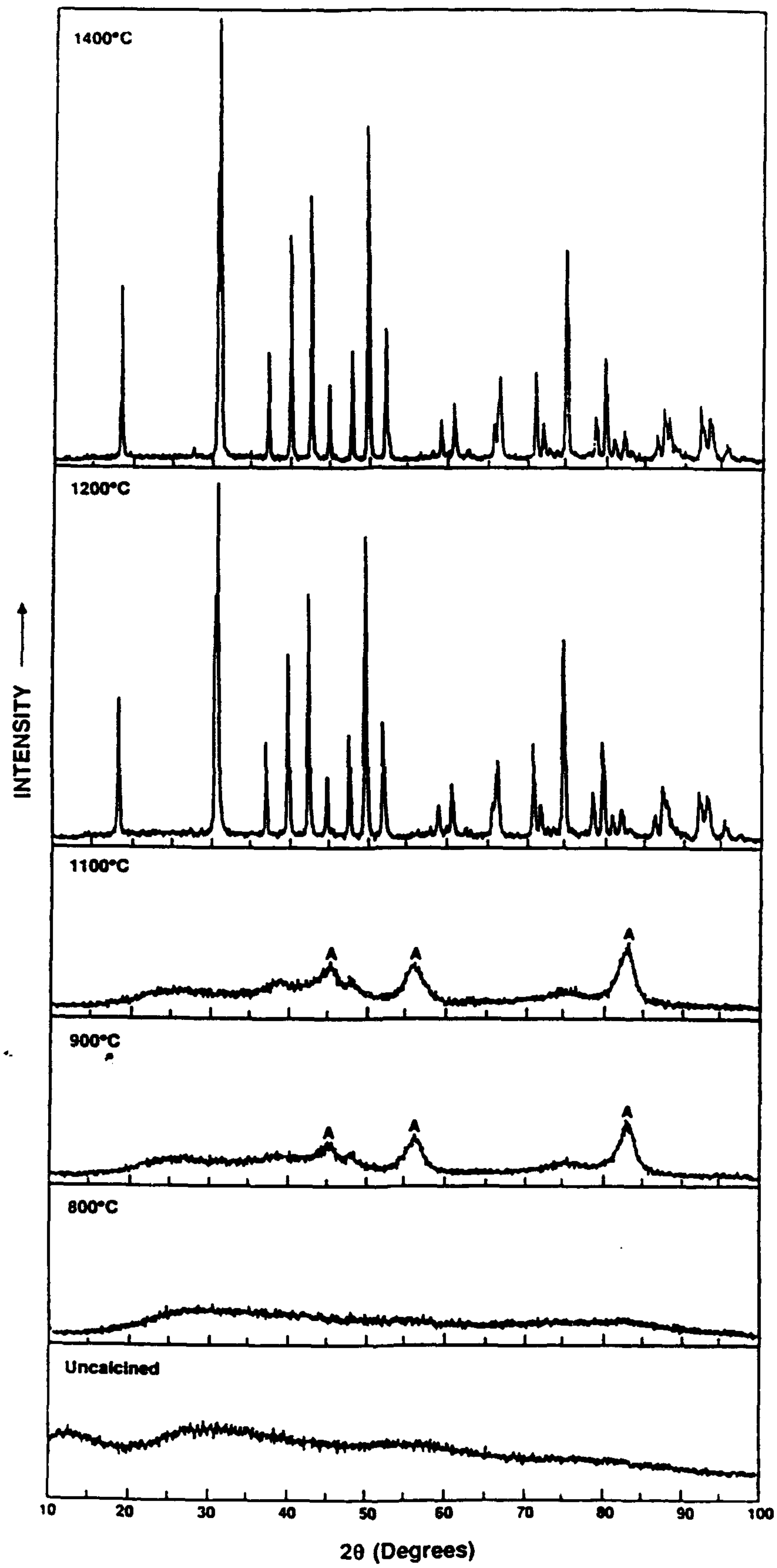
Mullite Fibers (Method #2)
(B)
WEIGHT (%)
100
80
60
40
20
0
0
200
400
600
800
1000
1200
1400
1600
TEMPERATURE (°C)


Mullite Fibers (Method #1)
SPECIFIC SURFACE AREA (m^2/g)
TEMPERATURE (°C)
(A)
0
20
40
60
80
100
120
400
600
800
1000
1200
1400
1600

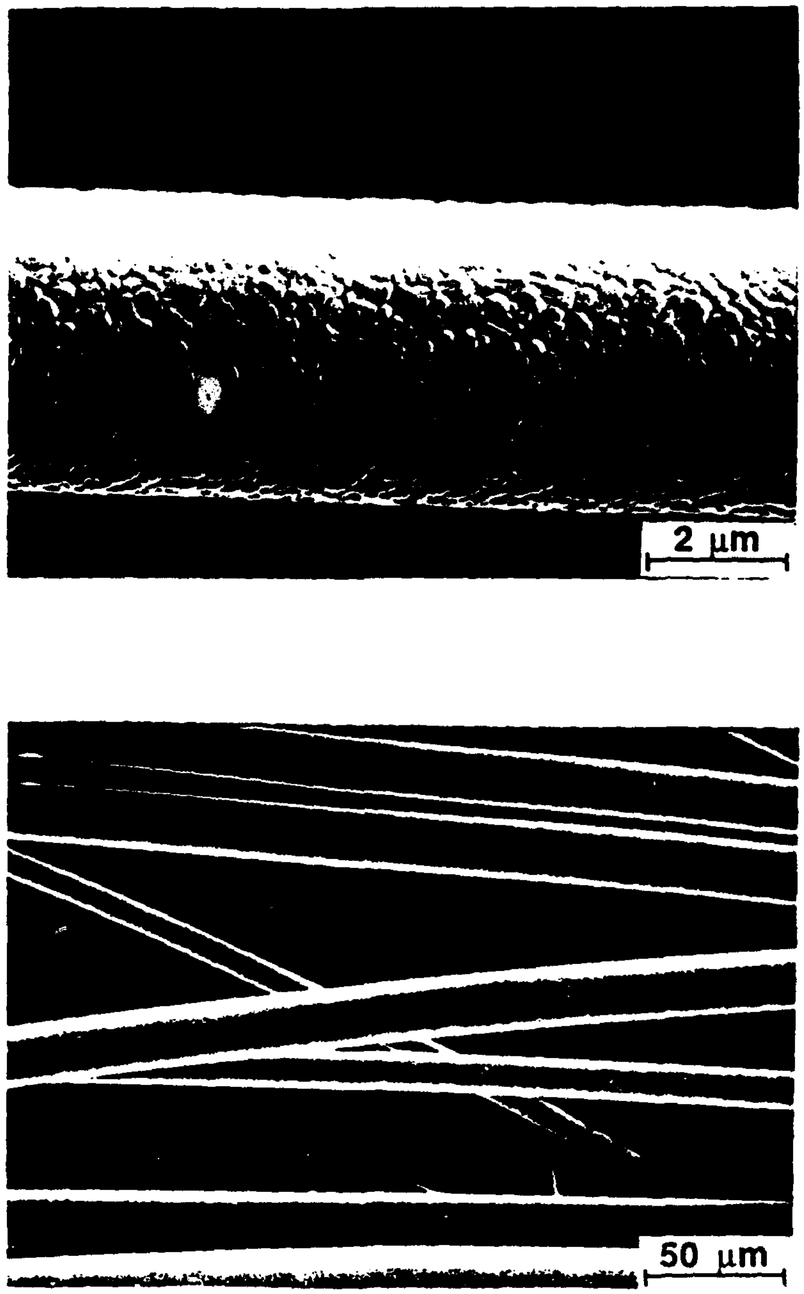

Mullite Fibers (Method #2)
SPECIFIC SURFACE AREA (m^2/g)
TEMPERATURE (°C)
(B)
0
40
80
120
160
200
240
400
600
800
1000
1200
1400
1600



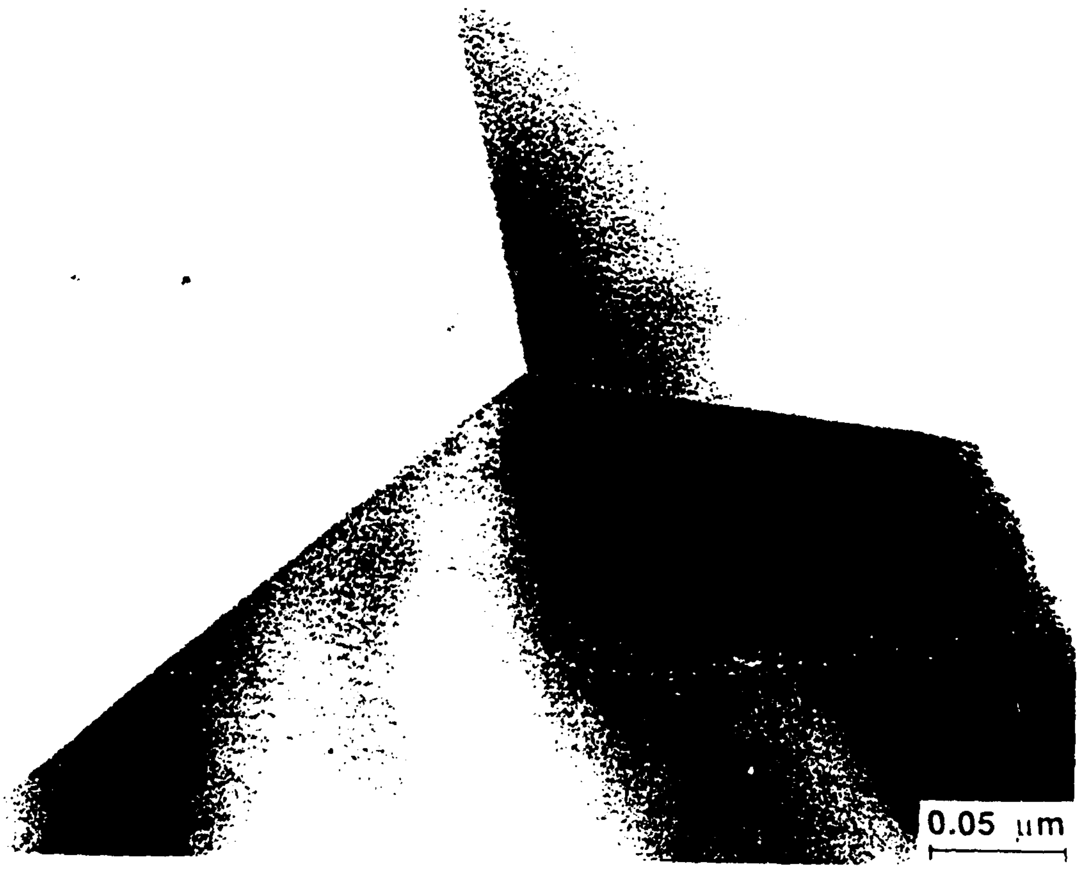
1400°C
1300°C
1200°C
A
A
A
800°C
A
A
A
600°C
A
Uncalcined
10
20
30
40
50
60
70
80
2θ (Degrees)


1400°C
1200°C
1100°C
900°C
800°C
Uncalcined
A
INTENSITY
10
20
30
40
50
60
70
80
90
100
2θ (Degrees)

Mullite Fiber (Method #1)



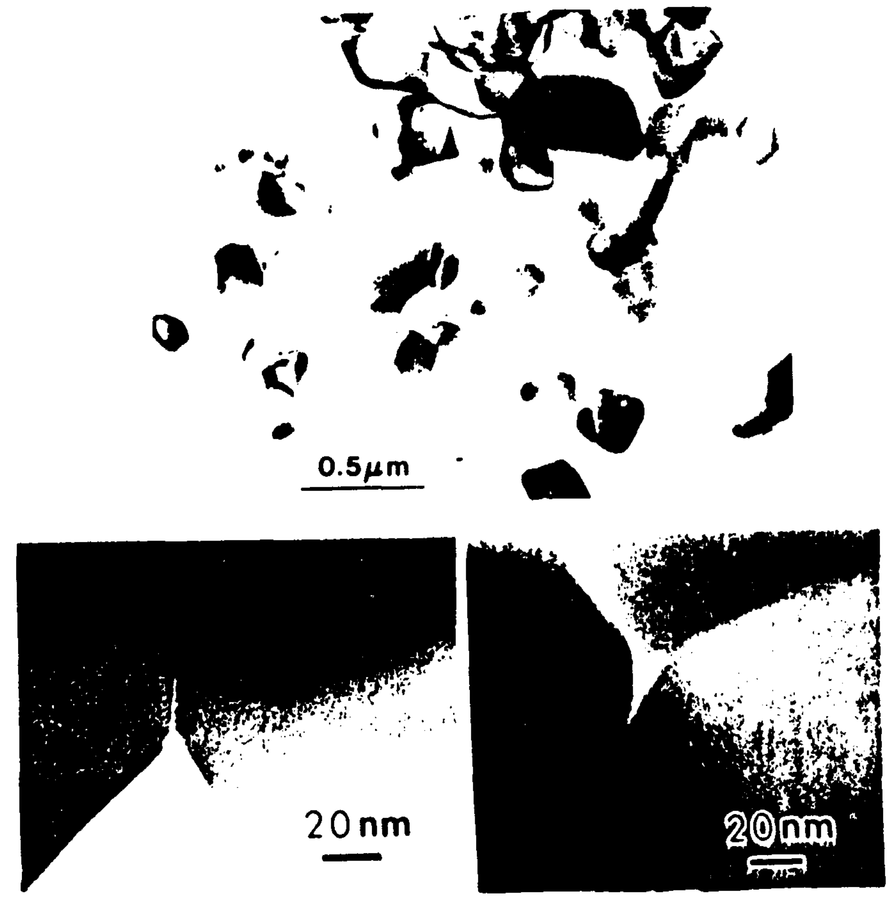
Mullite Fiber (Method #1)



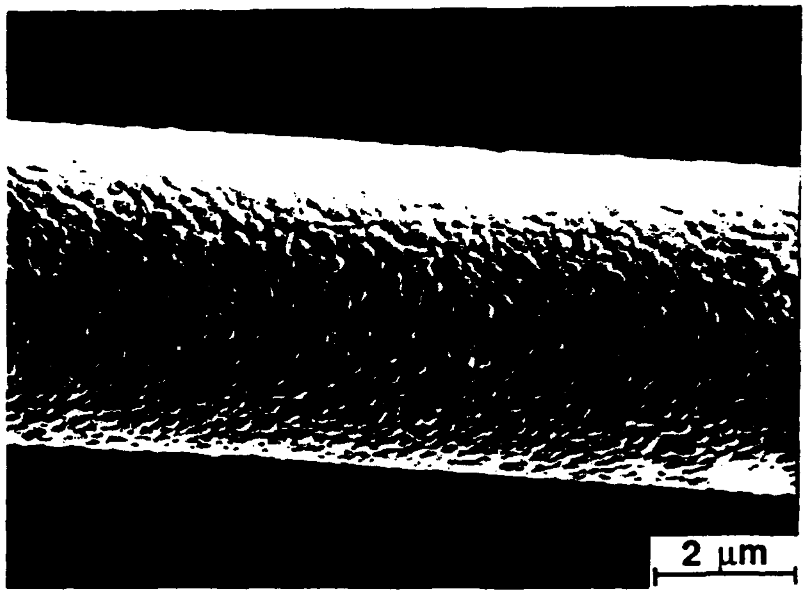
MULLITE BASED FIBERS (SOL-GEL PROCESS)

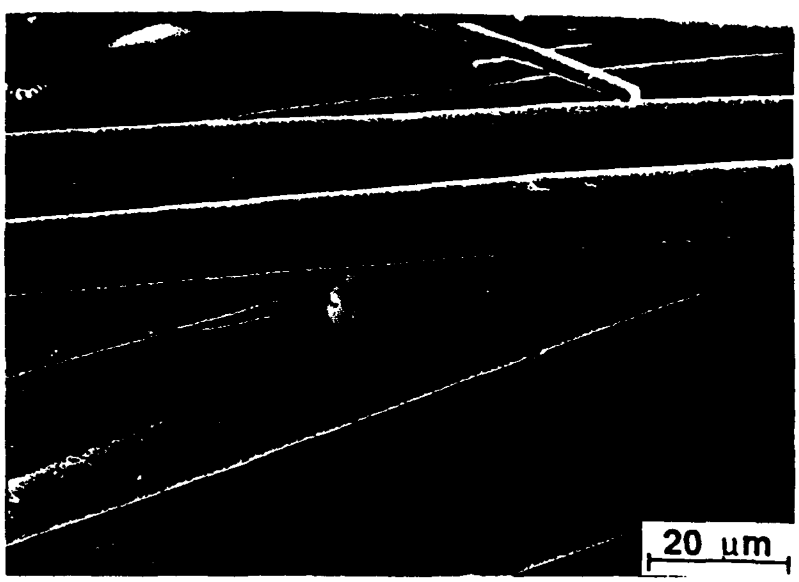
AI-CHLOROHYDROXIDE-SILICA SOL PRECURSOR, 1500°C

3M NEXTEL 480
AFTER 2hr. AT 1500°C

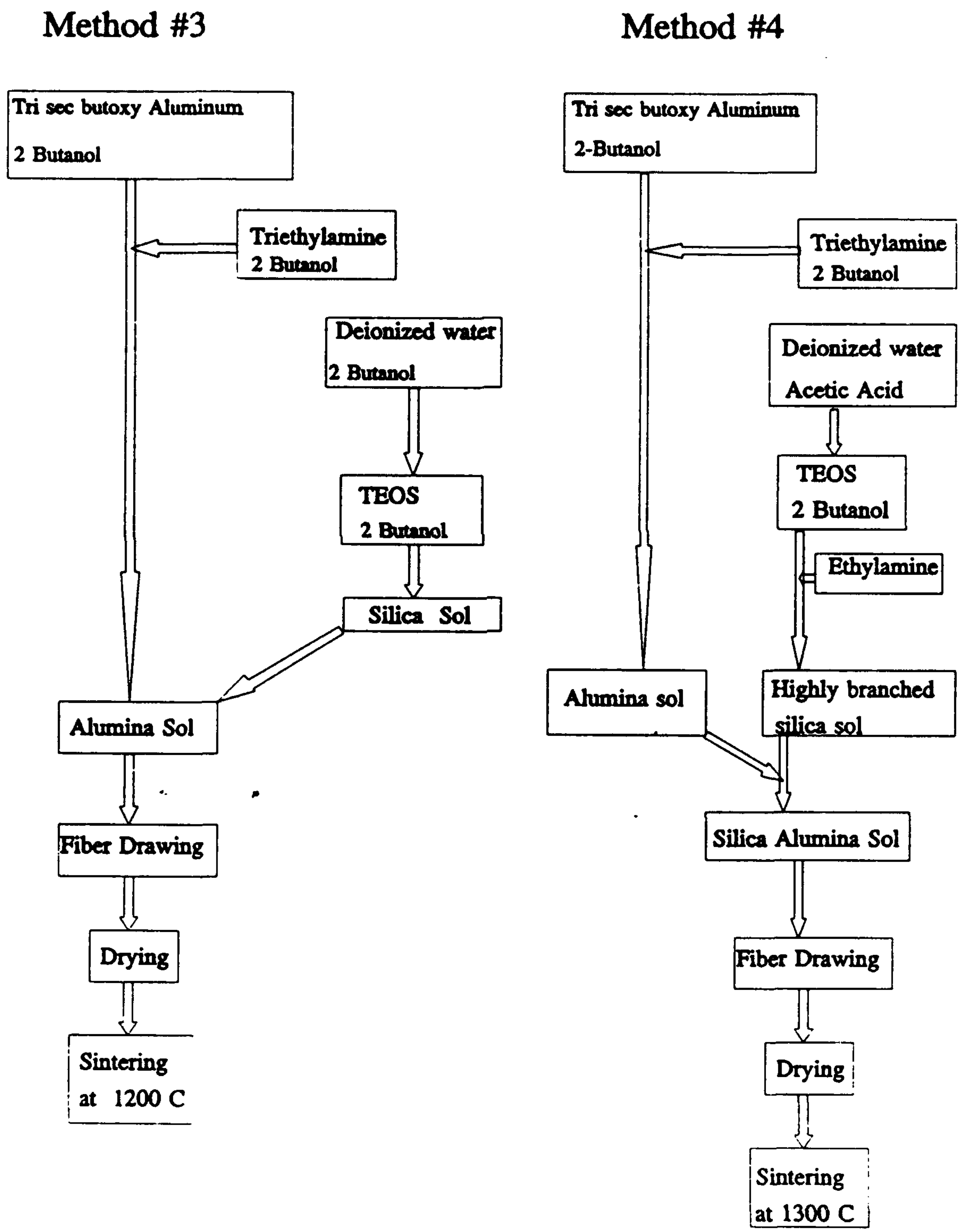


Mullite Fiber (Method #2)



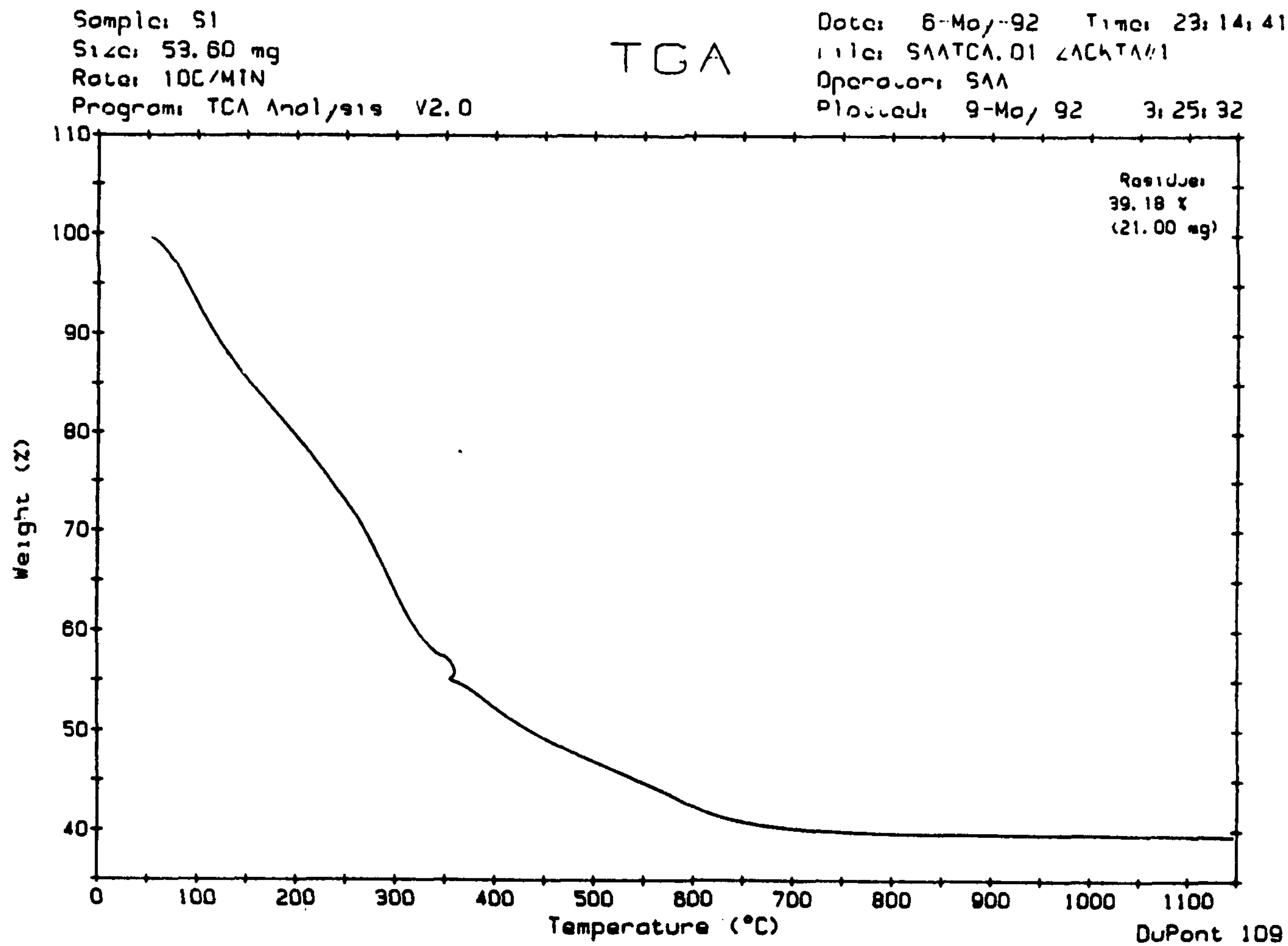


Silica Sol Methods

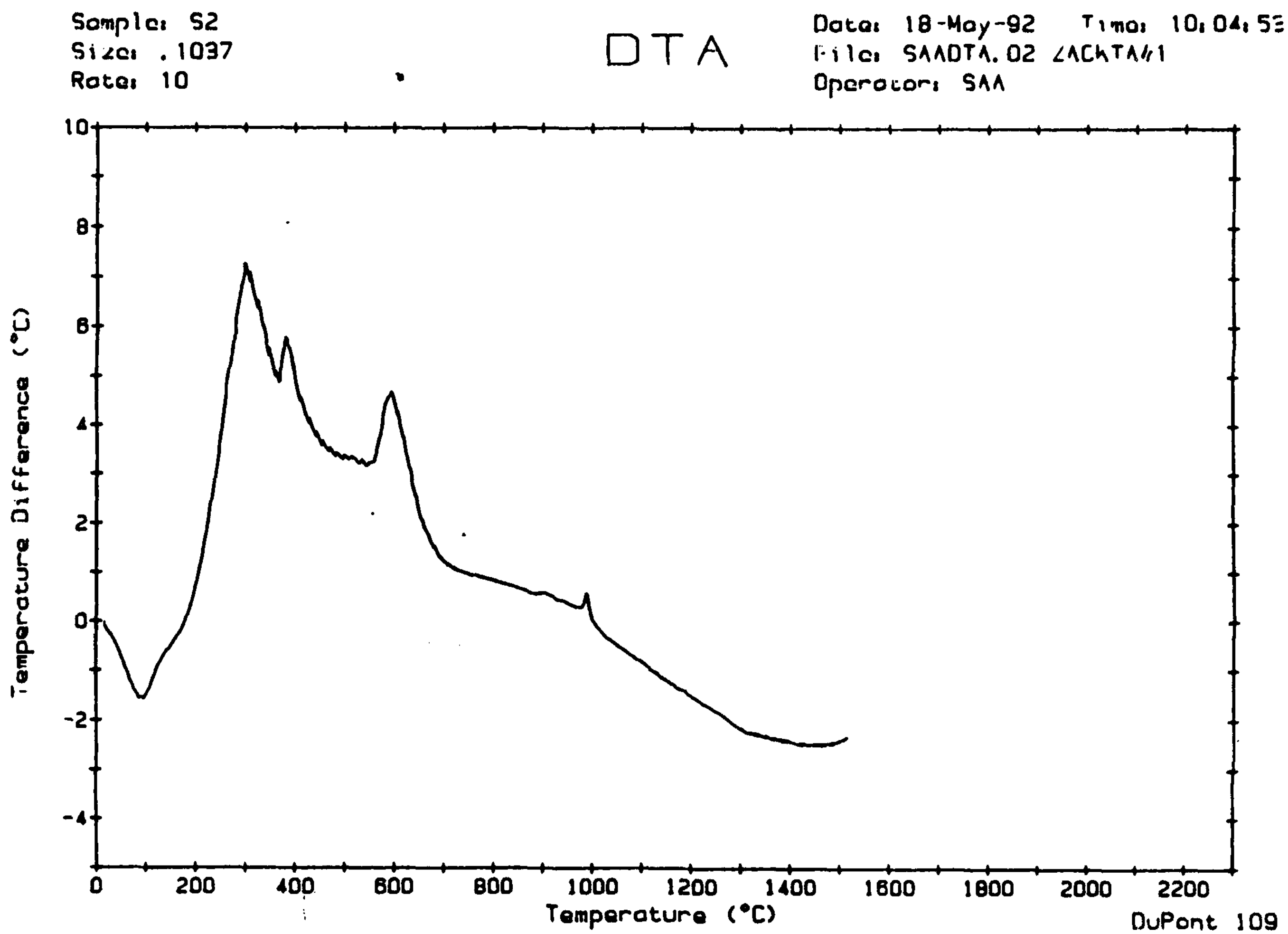


SILICA SOL METHODS

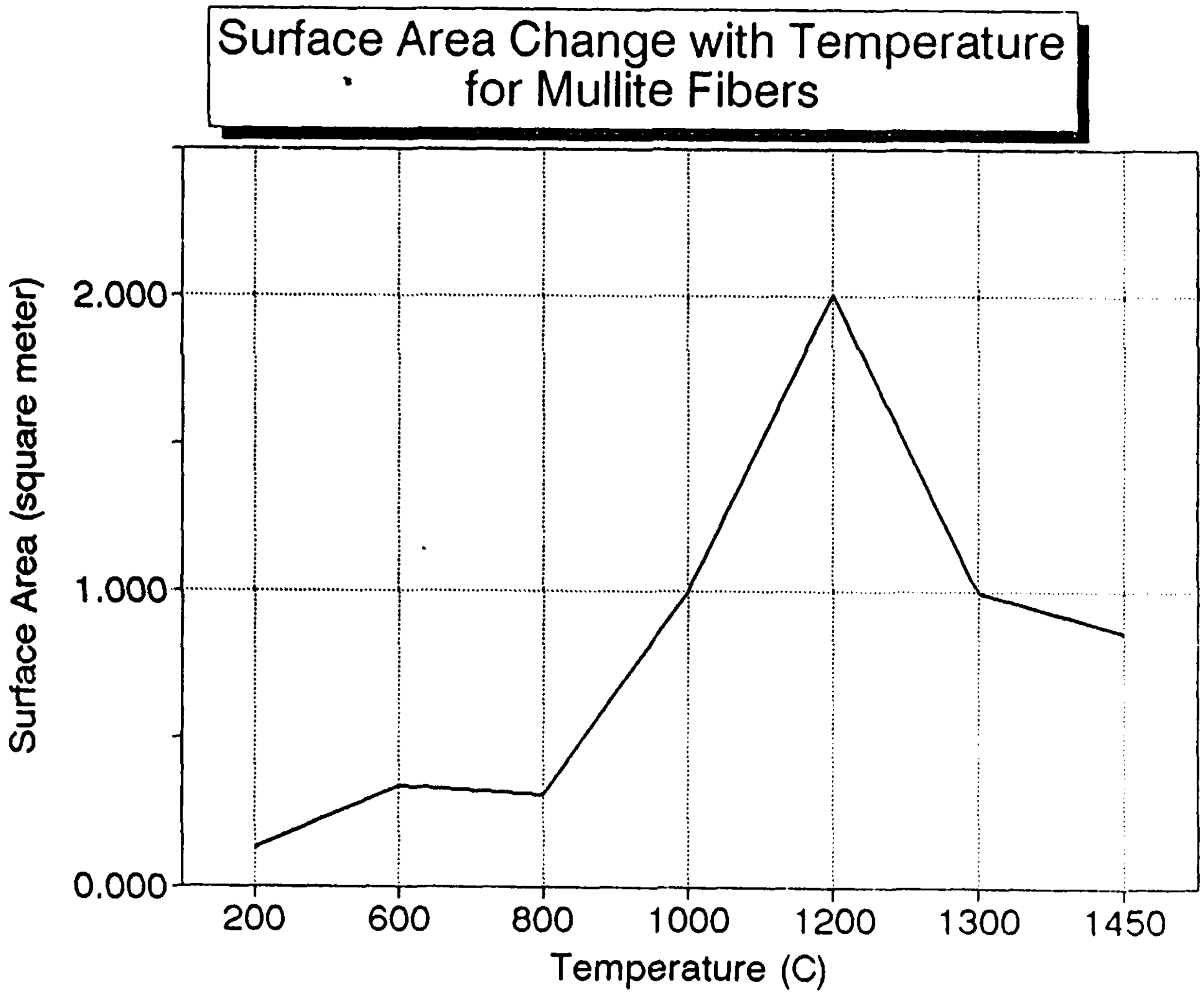
METHOD # 3



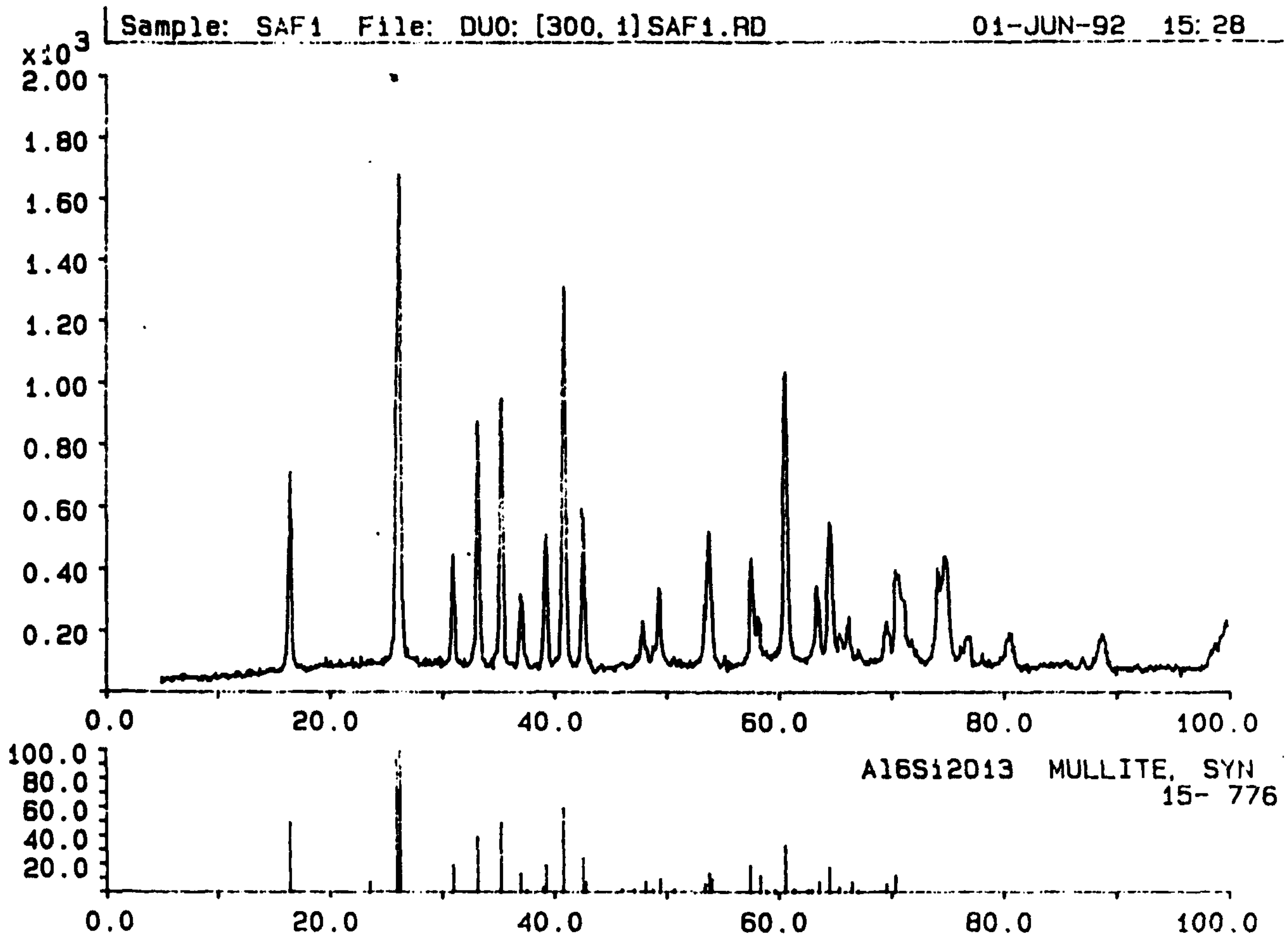
SILICA SOL METHODS
METHOD # 3



SILICA SOL METHODS
METHOD # 3



SILICA SOL METHODS
METHOD # 3



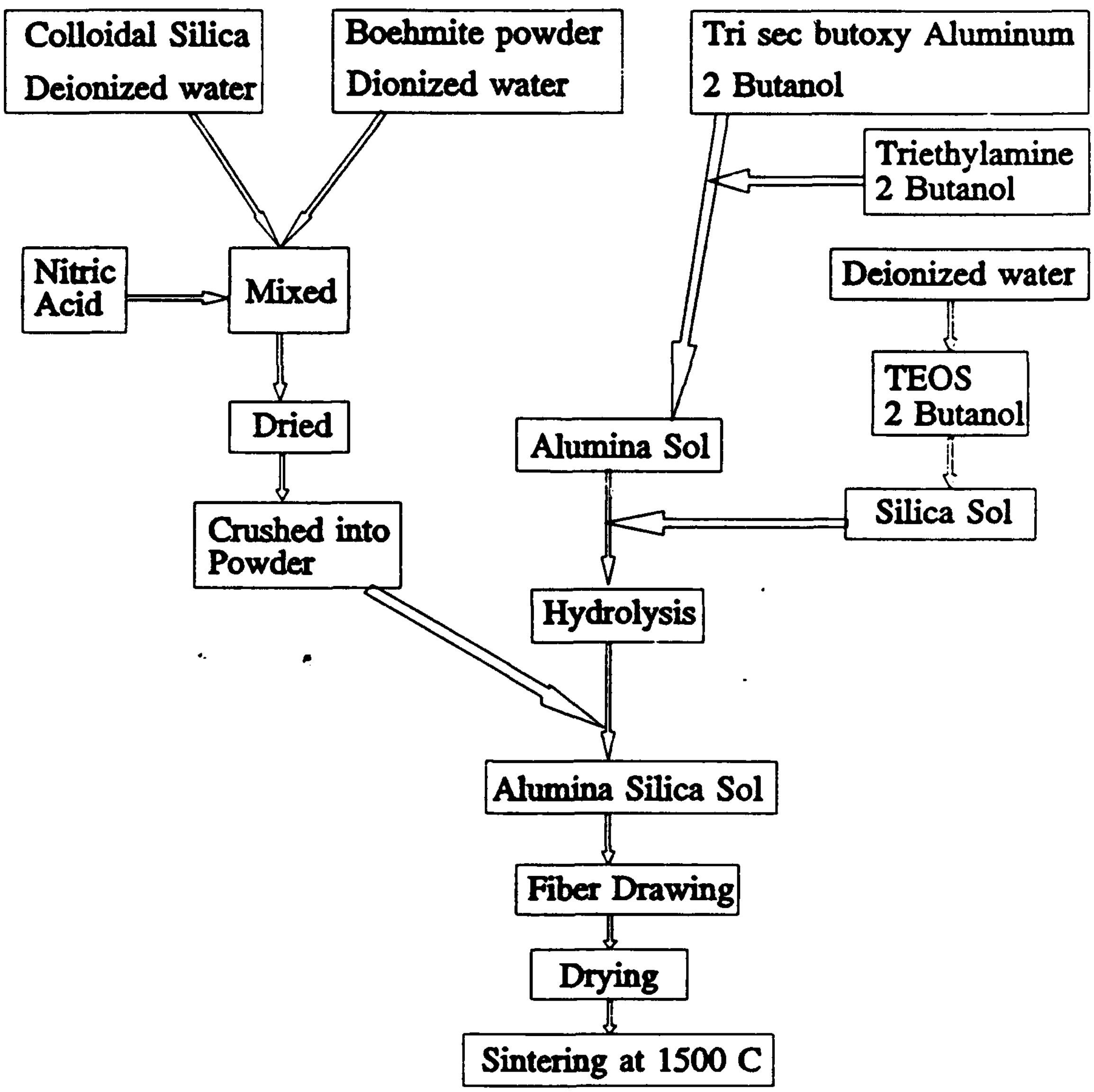
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

SOL-GEL APPROACHES FOR PRODUCING MULLITE

	Results:	Problems:
Colloidal Sols	Mullite phase formed (1200C) Full densification No intergranular glass phase Fine grain structure	Spinnability difficult to achieve
Polymer Sols	Mullite phase formed (1000C) Fine grain structure Spinnability excellent	Full density difficult to achieve
Seeded Sols	Promise: Full density No glass phase Spinnability Fine grain structure	Process control has many variables
Glass Leaching	Starts with woven blanket	Borate glass phase Process control

Seeded Sol Methods

Method #5



SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

A. GENERAL PROCESSING ISSUES

- Identified role of sol microstructure on mullite transition kinetics and sintering kinetics.
  - Colloidal silica retards mullite transition to 1250°C.
  - Colloidal silica enhances sintering kinetics below 1200°C.
  - Al-Si alkoxide precursors are mixed on the molecular scale and trigger the mullite transition at 980°C.
  - Early mullite transition has a detrimental effect on the sintering kinetics.

- Identified the role of sol microstructure on continuous fiber spinning.
  - Colloidal presursors have not produced adequate sols for continuous spinning.
  - Continuous spinning is achieved successfully when cross-linking of linear polymers occurs, as with alkoxide precursors.

- Identified formation of 6 $Al_2O_3 \cdot 1\ SiO_2$ spinel phase at 1000°C in the presence of alumina grains.
  - Spinel phase retards mullite transition to 1350°C.
  - Spinel phase liberates silica to allow for viscous phase sintering.

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

B. SPECIFIC RESULTS OF RESEARCH EFFORTS

- Colloidal Silica Methods (Methods #1, #2)
  - Formed fully dense mullite fibers
  - Formed structure with no intergranular glass phase
  - Formed sub-micron grain structure
  - Did not achieve continuous spinning
  - Centrifugal spun fibers were difficult to handle.

- Silica Sol Methods (Method #3)
  - Achieved continuous spinning of fibers
  - Spun fibers were processed up to 1450°C without handling problems
  - Formed mullite at 980°C
  - Resolved 2nd phase formation problem by improving polymer burn out below 600°C
  - Did not achieve full density at 1450°C
  - Formed 2-3 micron grain structure.

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

C. ONGOING STUDIES

- Colloidal Silica Methods
  - Addition of polydimethylsiloxane to form linear polymer structure as spinning aid
  - Formation of new Alumina sol precursors.

- Silica Sol Methods
  - Improved heating schedule to burn off carbonaceous residues and avoid formation of silicon carbide precipitates (this precipitate enhances glass phase formation upon decomposition of silicon carbide to silica)
  - Development of intermediate silica condensation process in basic solution (Method #4) to produce a more colloidal microstructure in the sol.

- Seeded Sol Methods (Method #5)
  - Studies of Boehmite seed volume fraction effect on intermediate spinel phase formation
  - Studies of the relationship of silica sol microstructure to sintering kinetics and full mullite conversion
  - Studies of tolerance of spinning process for partial colloid addition.

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

D. FUTURE WORK

- Full scale investigation of seeded sol methods
- Strength tests vs processing conditions
- High temperature mechanical tests
- Modification of spinning process to include on-line heat treatment processes
- Development of on-line tests for AI controlled processing.

CHEMICAL VAPOR DEPOSITION APPROACHES TO IMPROVED COMPOSITE STRUCTURES

Tim Anderson

Chemical Engineering Department

DARPA

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

OBJECTIVES

- Develop chemical vapor infiltration (CVI) processes for densifying composite structures
- Develop CVD processes for coating applications

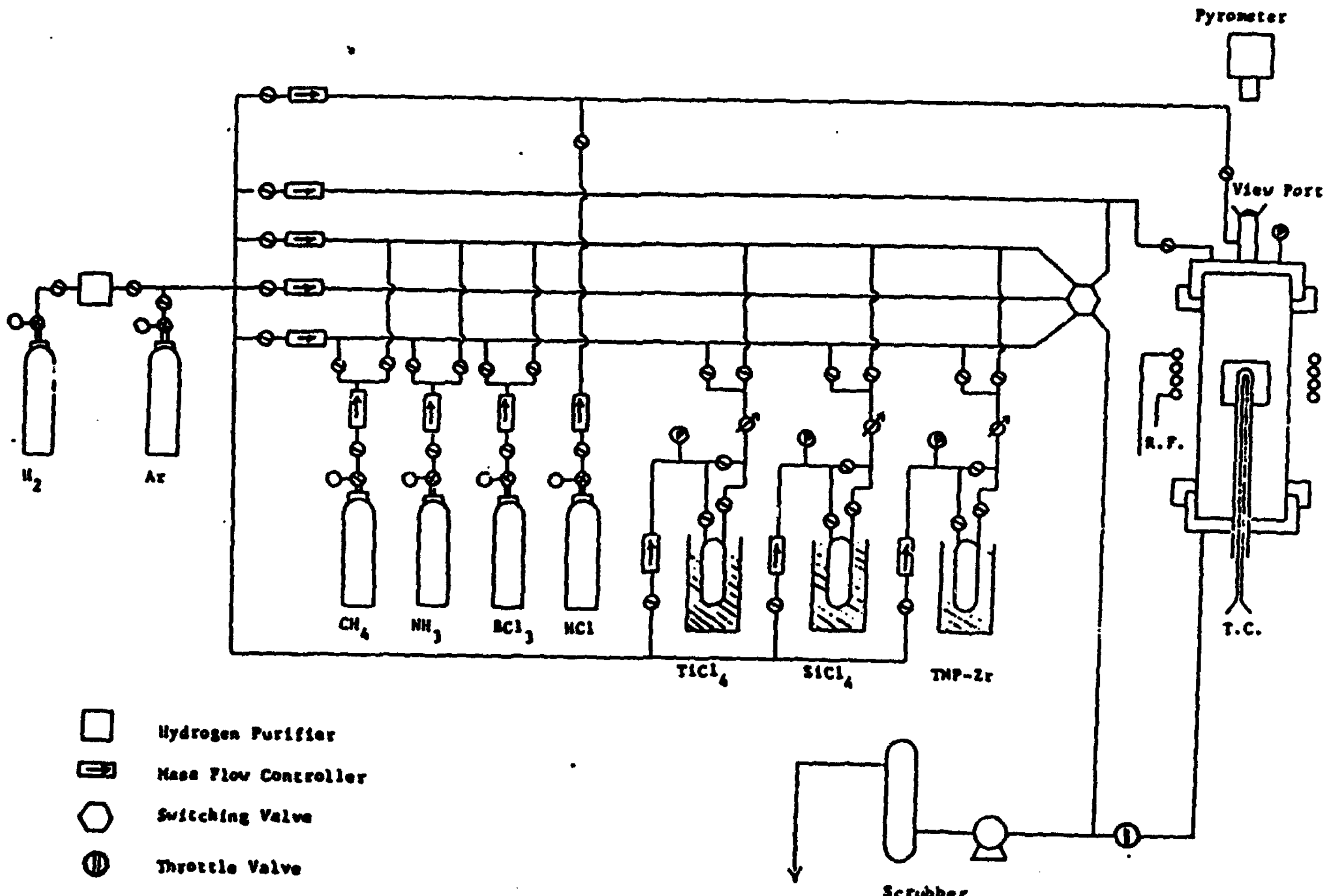
  control interfacial bonding, reactivity and diffusion
  improve mechanical properties
  increase wetting by metals
  improve polishibility

APPROACHES

- Construct general purpose cold-wall CVD system
- Understand deposition chemistries and mechanisms
- Investigate novel rector designs for CVI
- Explore atomic layer deposition (ALD) mode

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

New CVD Schematic
Low Pressure, Fast-Switching Manifold, Multiple Species



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System Features

- Four Independent Gaseous Sources (Currently BCl_3, SiH_2Cl_2, CH_4 and NH_3 or HCl)
- Three Independent Liquid Sources (Currently $TiCl_4$, $SiCl_4$ and PCl_3)
- Computer Operated Mass Flow Controllers
- Pressure Control
- Rapid Switching Run-Vent Radial Manifold
- Impining-Jet Flow Reactor Design

System Capabilities

- Various Carbide, Nitride, Boride and Silicide Chemistries
- Compositional Grading
- Multilayer Structures
- In-situ Chemical Etching
- Extended-Time Atomic Layer Deposition

DARPA

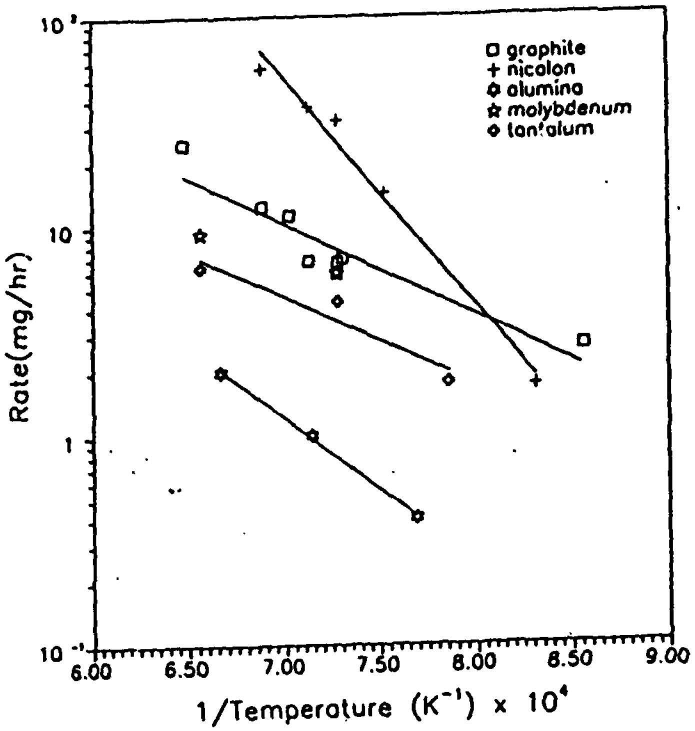
TiC Properties

- High melting temperature (2940°C)
- High microhardness (2000-3000 GPa)
- High transverse rupture strength (240-400 GPa)
- Wear resistant
- Oxidation resistant

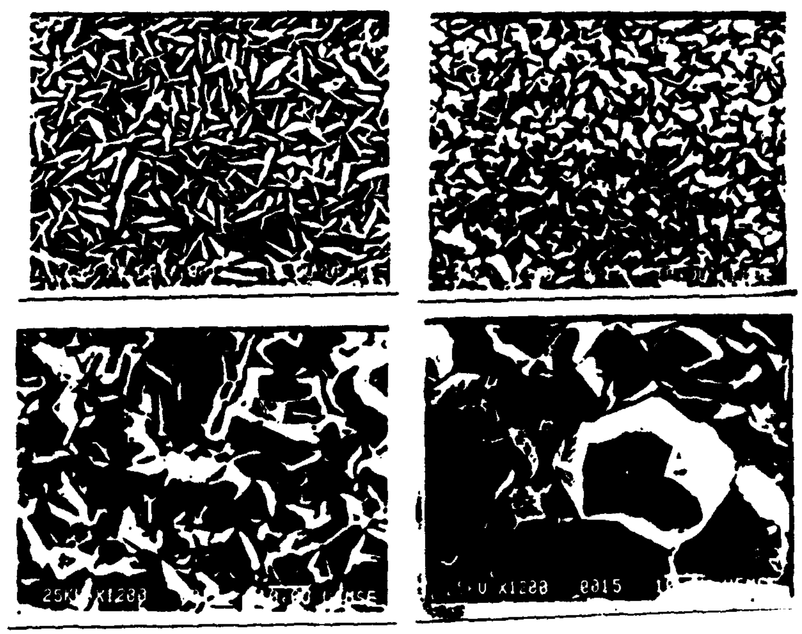
Applications

- Protective coatings on steels, ceramic inserts and bulk ceramic cutting tools
- Matrix phase in hybrid carbon/carbon composites
- High temperature applications

REACTION LIMITED DEPOSITION OF TiC_x



Growth rate of TiC_x on various substrates as a function of reciprocal temperature.



Microstructure of TiC_x on Alumina, clockwise from upper left-hand side corner, T=1300 °C and $CH_4/TiCl_4$= 0.5, T= 1300°C and $CH_4/TiCl_4$=1.0, T= 1300°C and $CH_4/TiCl_4$=3, T= 1300°C and $CH_4/TiCl_4$=4.0.

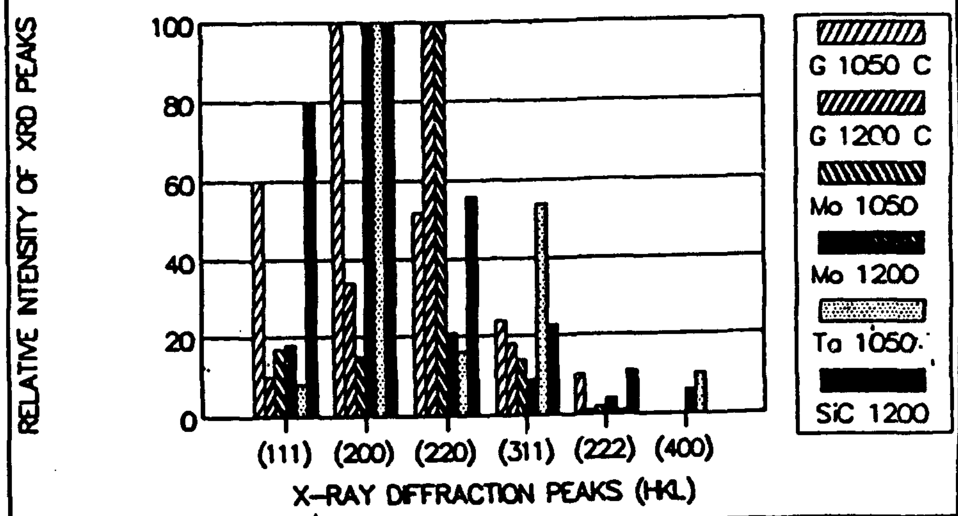
COMPARISON OF ACTIVATION ENERGY AND ORIENTATION FOR DEPOSITION OF TiC_x

SUBSTRATE	EA(KJ/MOL)
Al_2O_3	130
GRAPHITE	109
NICALON	210

PREFERRED ORIENTATIONS

SUBSTRATE	T(°C)	(HKL)	T(°C)	(HKL)
GRAPHITE	1050	(200)	1200	(220)
NICALON	1050	(200)	1200	(200)
Al_2O_3	1050	(111)	1200	(111)
Mo	1050	(220)	1200	(200)
Ta	1050	(200)	------	

PREFERRED ORIENTATIONS OF TiC GROWN ON DIFFERENT SUBSTRATES

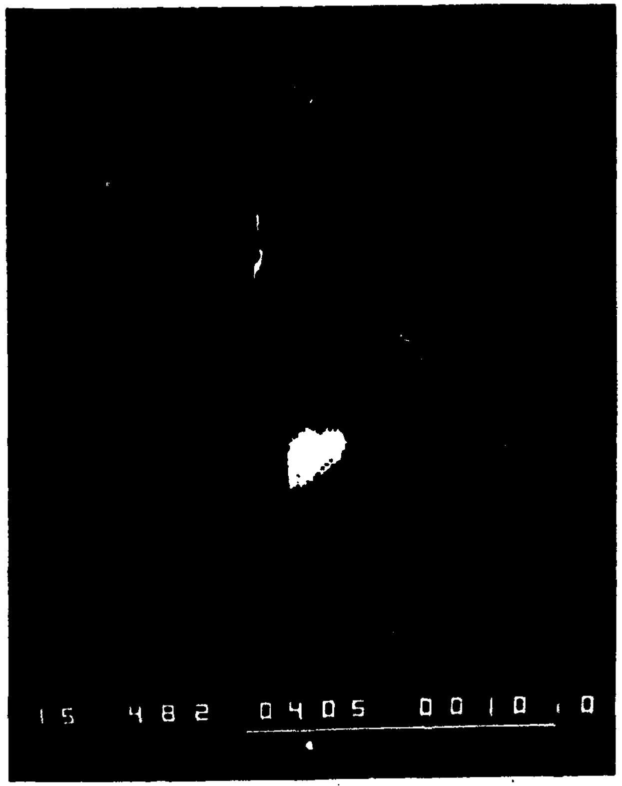


DARPA

Microhardness and Fracture Toughness of CVD TiC_x

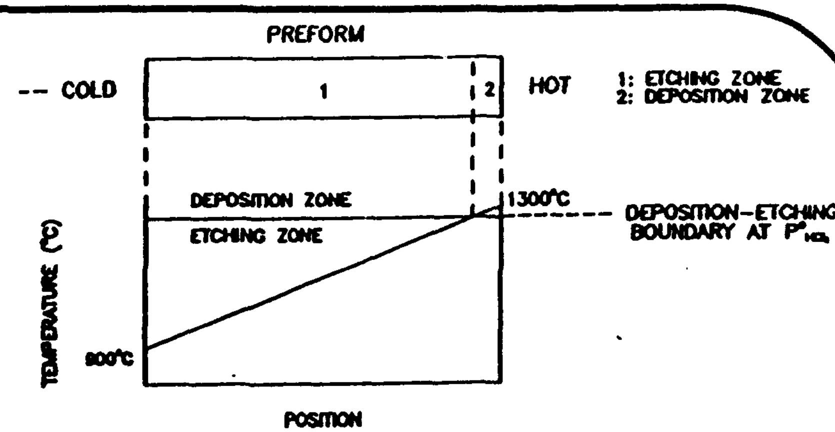
Deposition Temperature	Graphite		Nicalon	
T (°C)	H (GPa)	K_c ($MPa \cdot m^{1/2}$)	H (GPa)	K_c ($MPa \cdot m^{1/2}$)
1050	21	3.5	22	2.6
1200	27	2.1	26	2.1

- Increasing the deposition temperature increases the hardness and decreases the fracture toughness of the TiC matrix. Increased cracking is observed at deposition temperatures of > 1100°C.

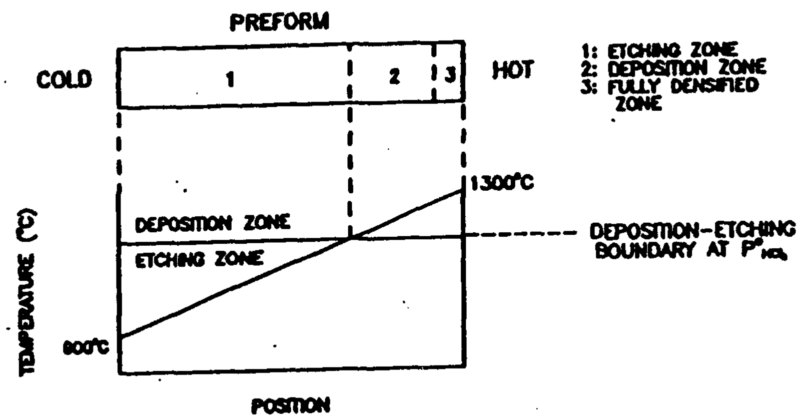


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

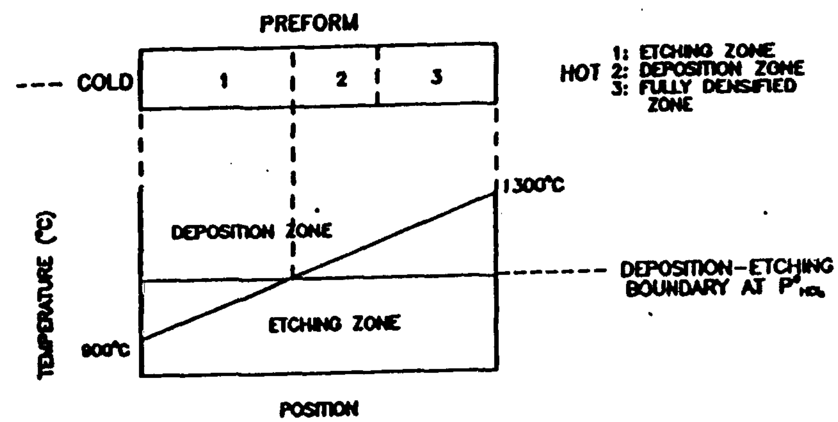
CVI WITH THERMAL GRADIENT AND HCL FLOW CONTROL



2-38 CVI BY THERMAL GRADIENT AND HCL ETCHING. P^{o}_{HCl} IS THE INITIAL INLET PARTIAL PRESSURE OF HCL.

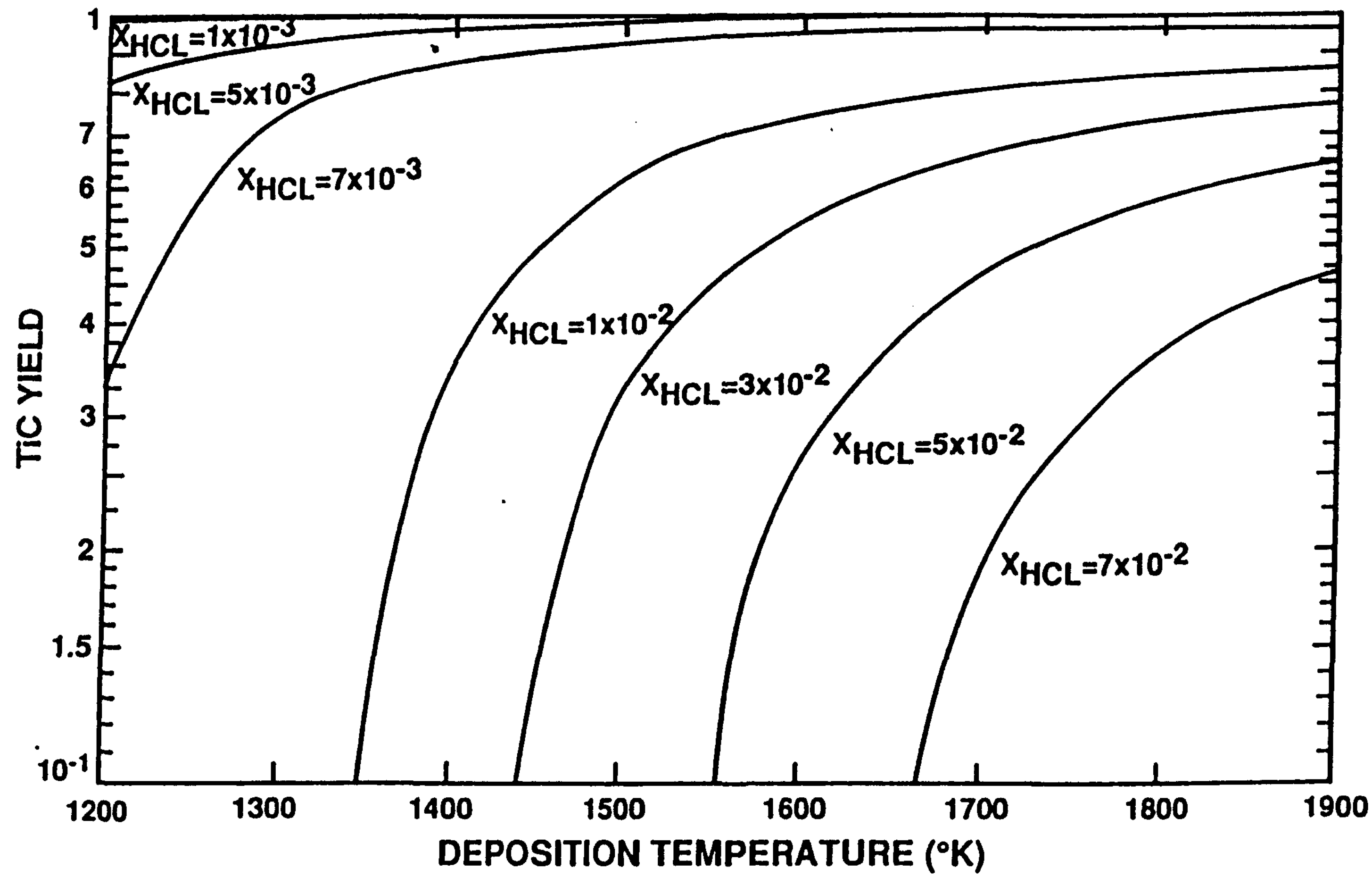


2-39 CVI BY THERMAL GRADIENT AND HCL ETCHING. P^{o}_{HCl} IS LESS THAN P^{o}_{HCl}



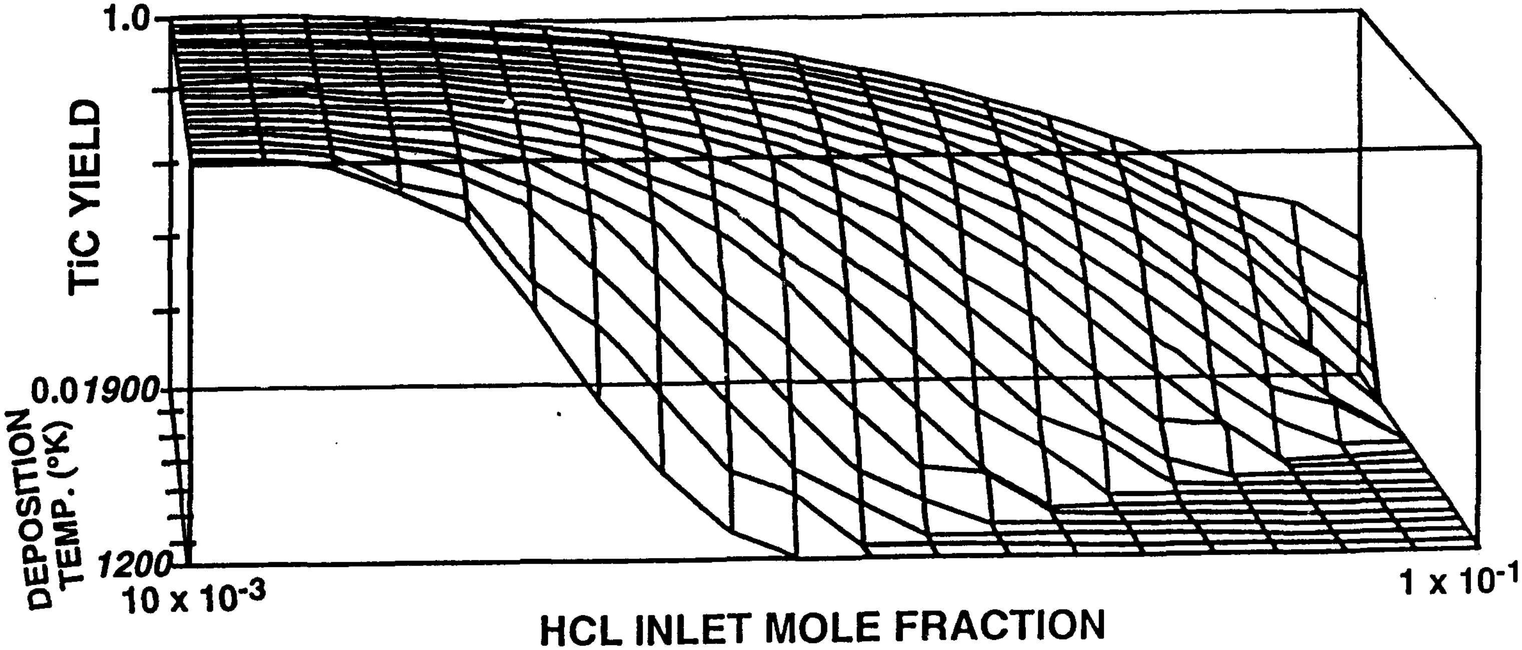
2-40 CVI BY THERMAL GRADIENT AND HCL ETCHING. P^{o}_{HCl} LESS THAN P^{o}_{HCl}

TiC YIELD vs DEPOSITION TEMPERATURE and HCl CONCENTRATION



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

TiC YIELD vs. TEMPERATURE and HCl CONCENTRATION



CH_4 Inlet Mole Fraction = 0.01
$TiCl_4$ Inlet Mole Fraction = 0.0001

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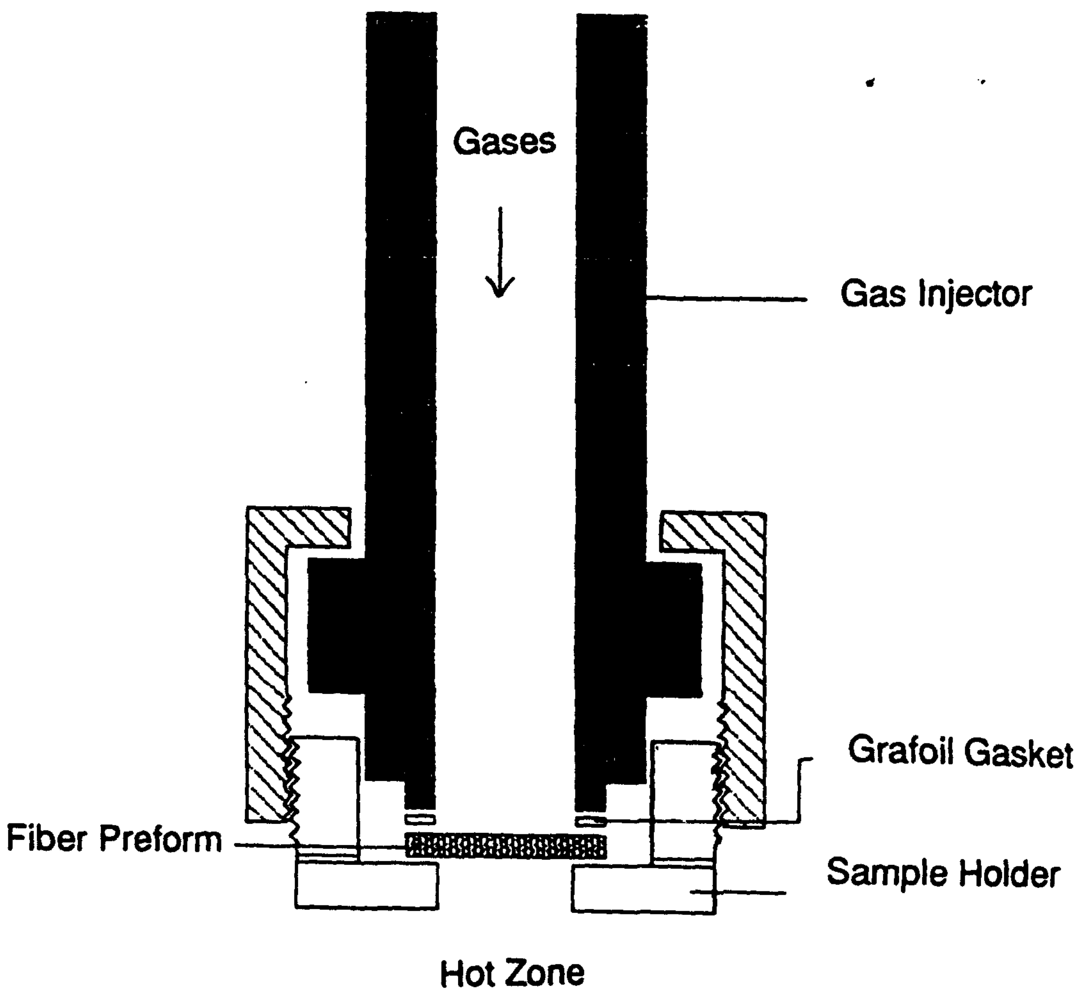
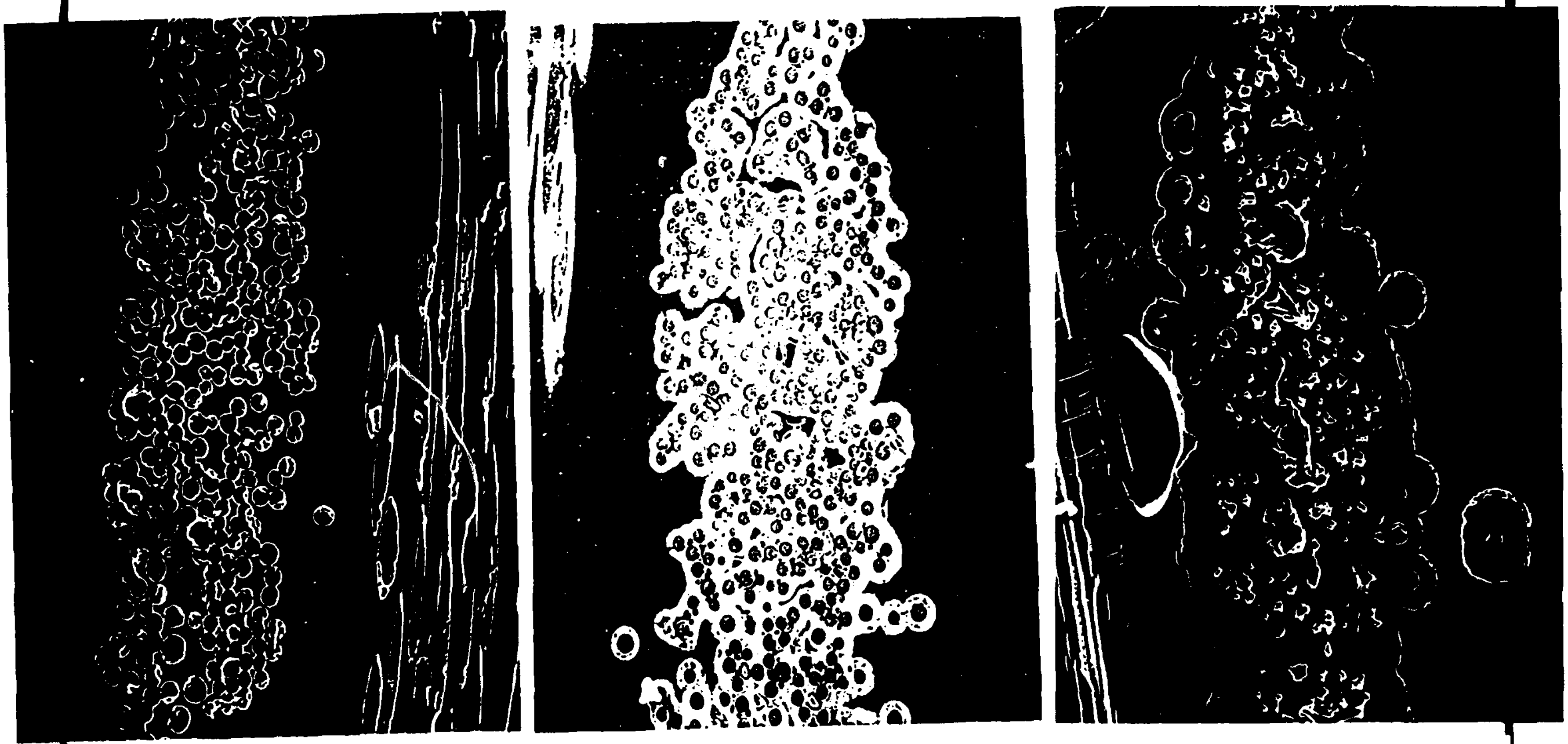
Sample Holder Set-up For Forced-flow Temperature-Gradient CVI



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

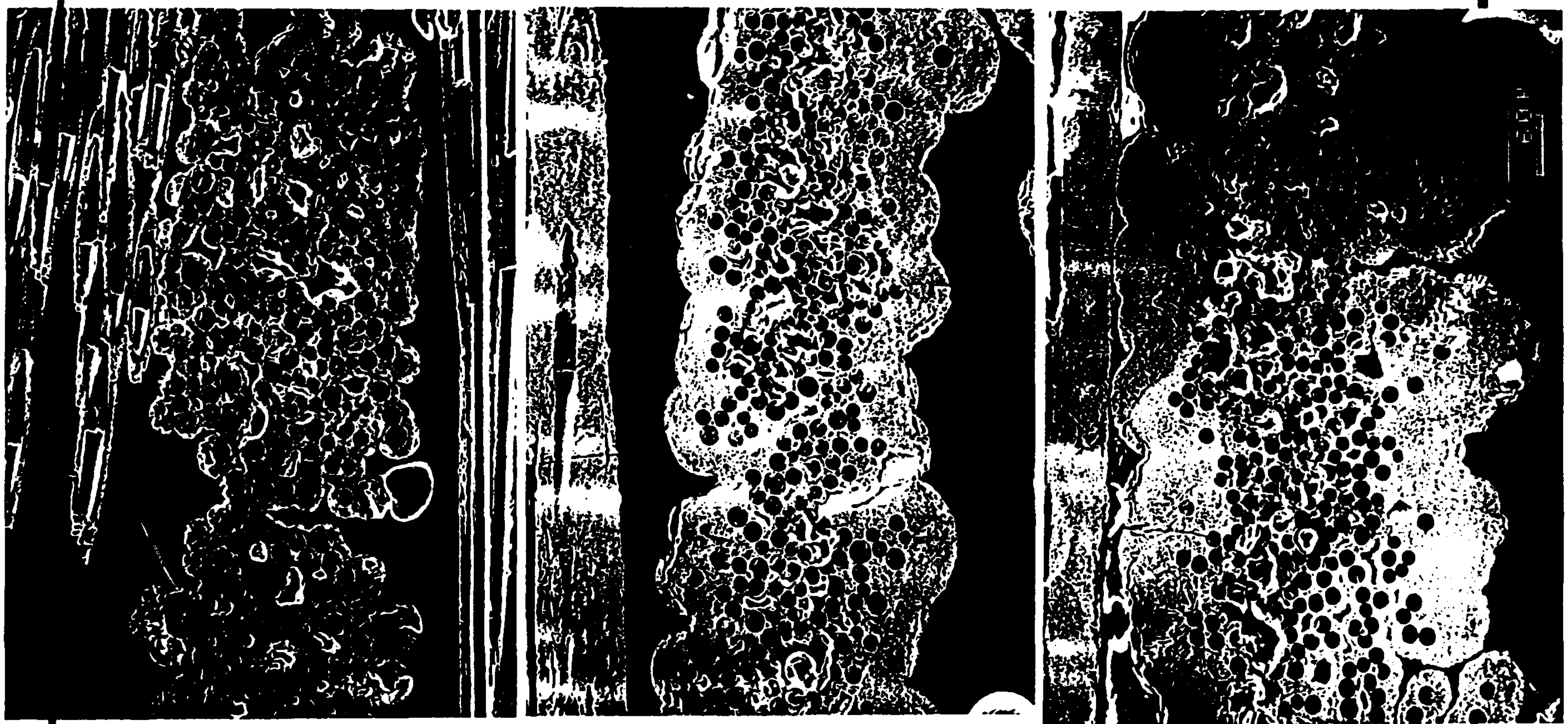
CONVENTIONAL CVI AT LOWER C/Ti RATIO (2/1)



Top Layer (1000°C) Middle Layer Bottom Layer (1300° C)

INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Conventional Forced-flow CVI of a Nicalon Preform with TiC_x.



Top Layer (1000°C) Middle Layer Bottom Layer (1300° C)

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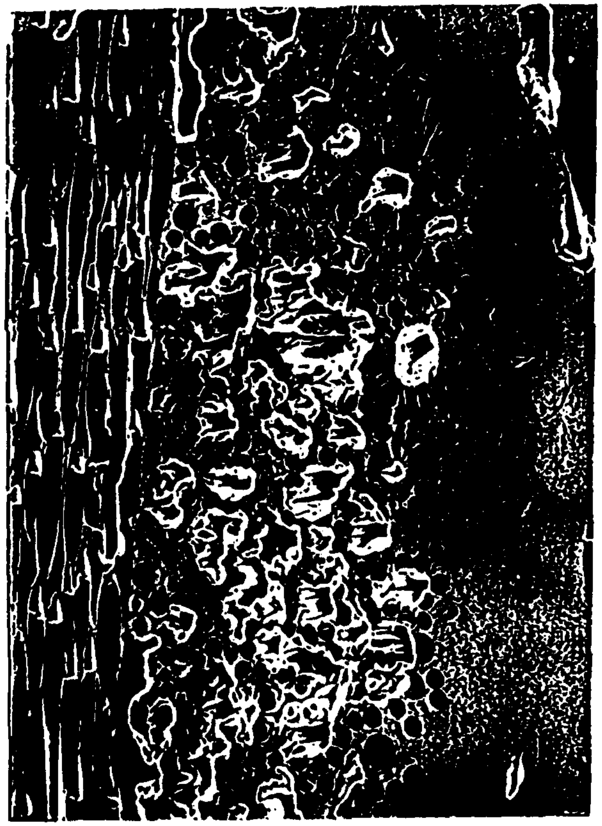
FORCED-FLOW CVI COUPLED WITH HCL ETCHING

Top Layer (1000°C)



Middle Layer

Bottom Layer (1300°)

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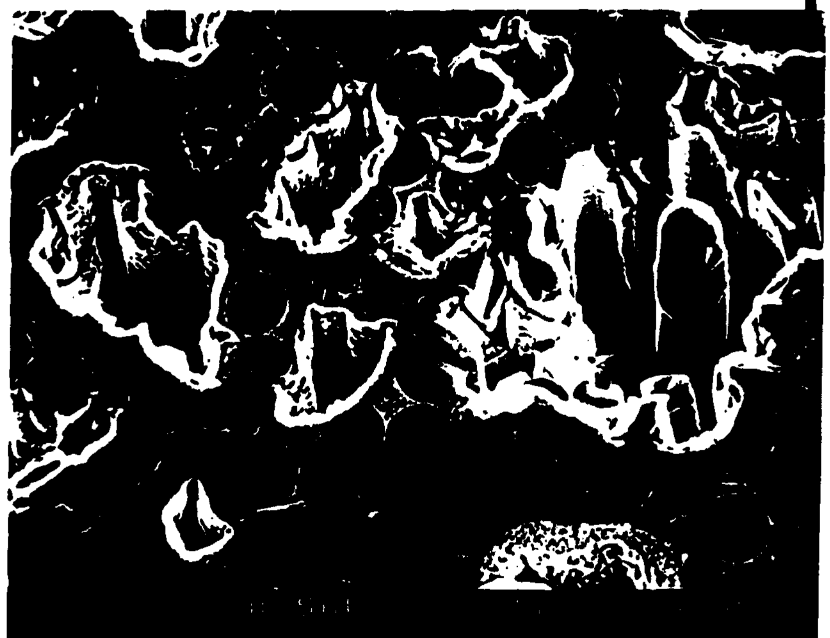
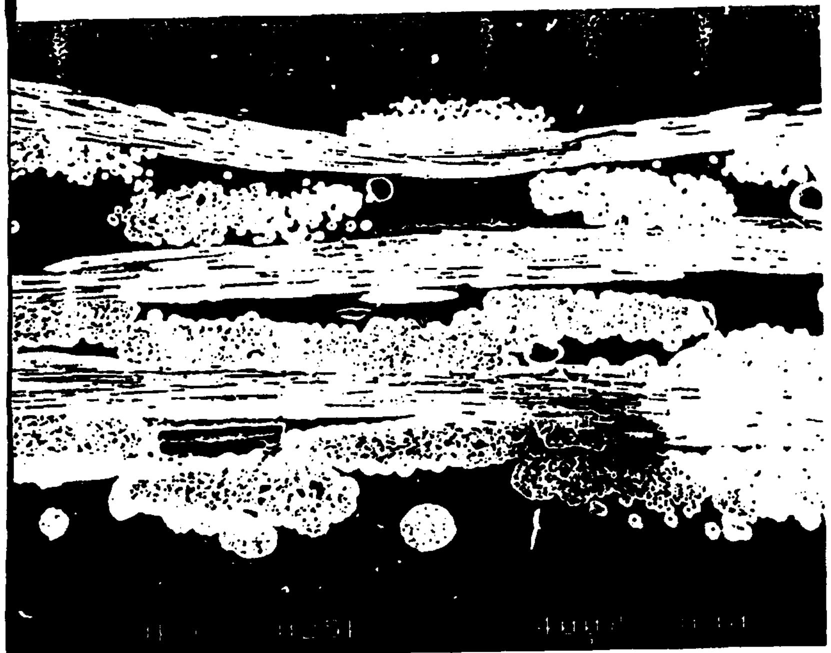
ULTRA-HIGH TEMPERATURE APPLICATIONS

FIBER PULL-OUT AFTER POLISHING
INFILTRATED NICALON PREFORM



COMPARISON OF CVI PROCESSES



Conventional Forced-flow CVI
of a Nicalon Preform with TiC_x

Forced-flow CVI coupled with
HCl injection

Silicon Carbide Deposition Parameters

Temperature..........1523K
Pressure..........200 torr
Inlet Gas Conditions
- SiH_2Cl_2..........40 sccm
- CH_4..........40 sccm
- H_2..........420 sccm

Time..........45 min.
Film Thickness..........100+ µm
Substrate..........Si (100)

Carburization Parameters

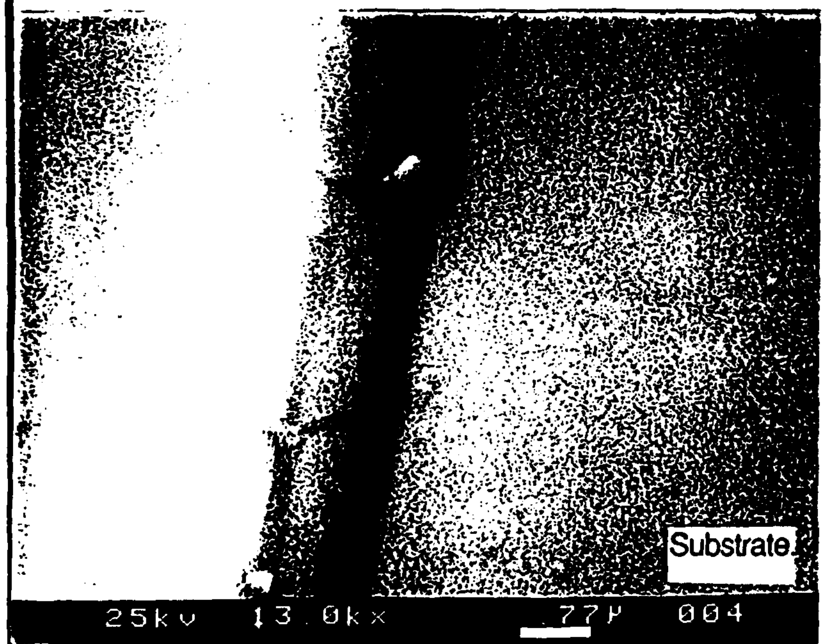
Done Immediately Prior to SiC Deposition

Temperature..........1523K
Pressure..........200 torr
Inlet Gas Conditions
- CH_4..........10 sccm
- H_2..........420 sccm

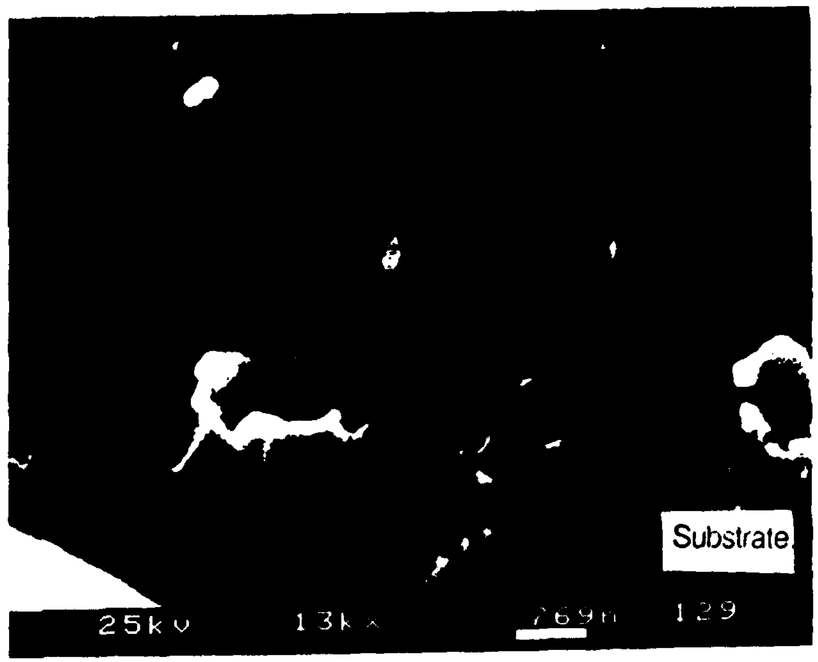
Time..........10 min.
Film Thickness (est.)..........1 µm

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Interface Without Carburization



Interface With Carburization



1 μm

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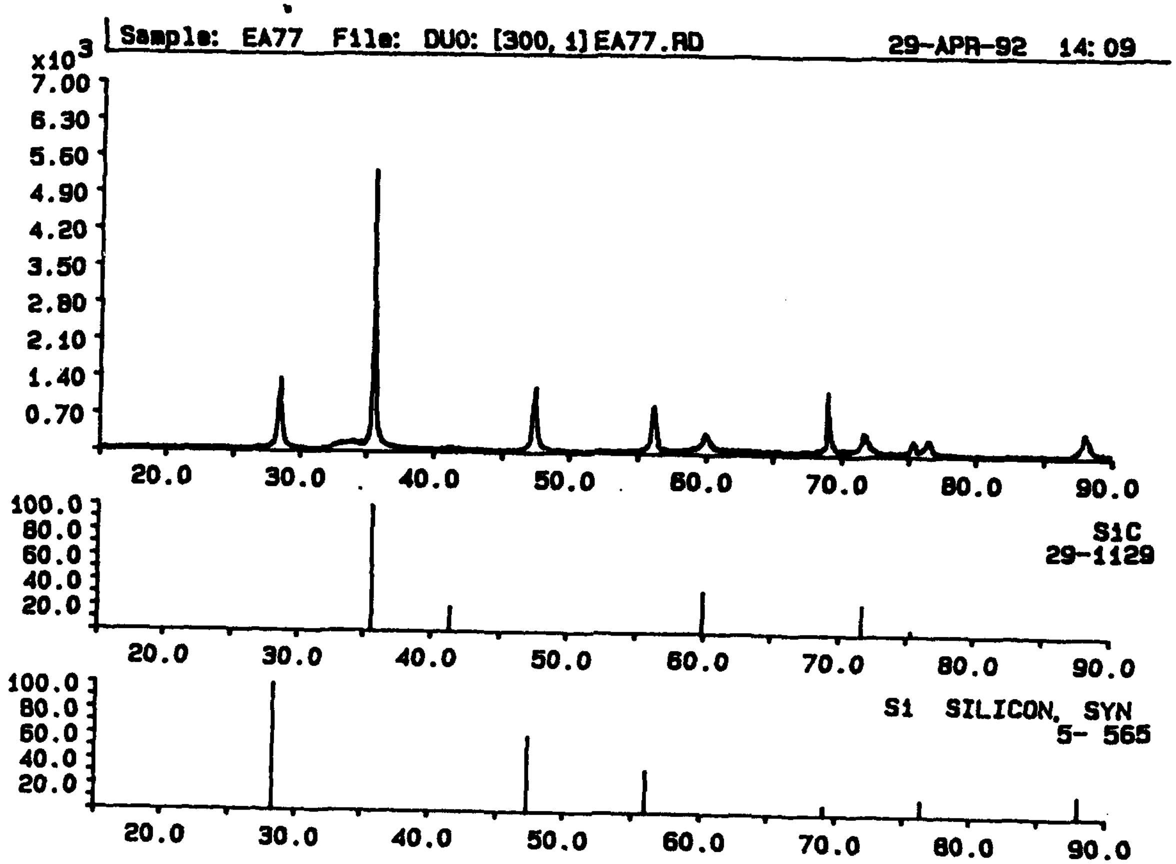
With Carburization



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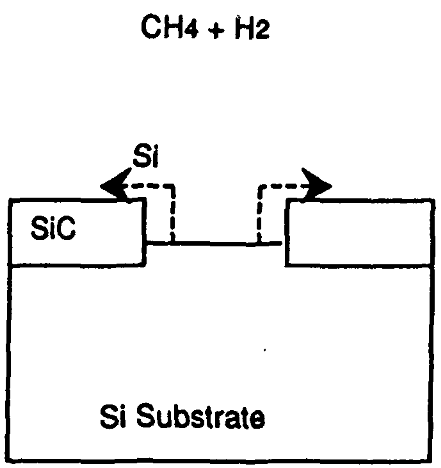
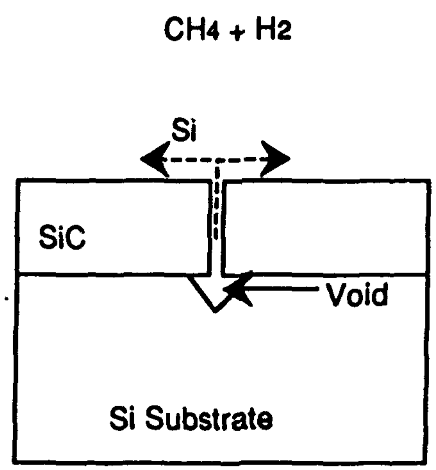
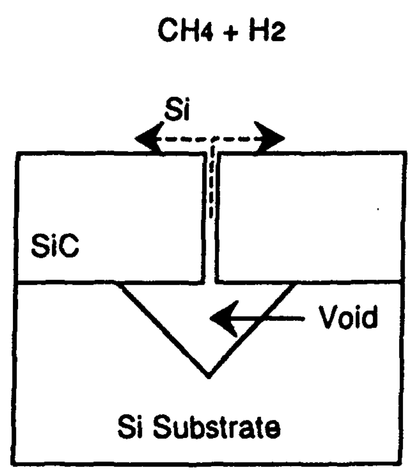
Void Formation During Carburization



Nucleation and 3D Growth:
Uncovered areas provide silicon at growth interface via surface diffusion

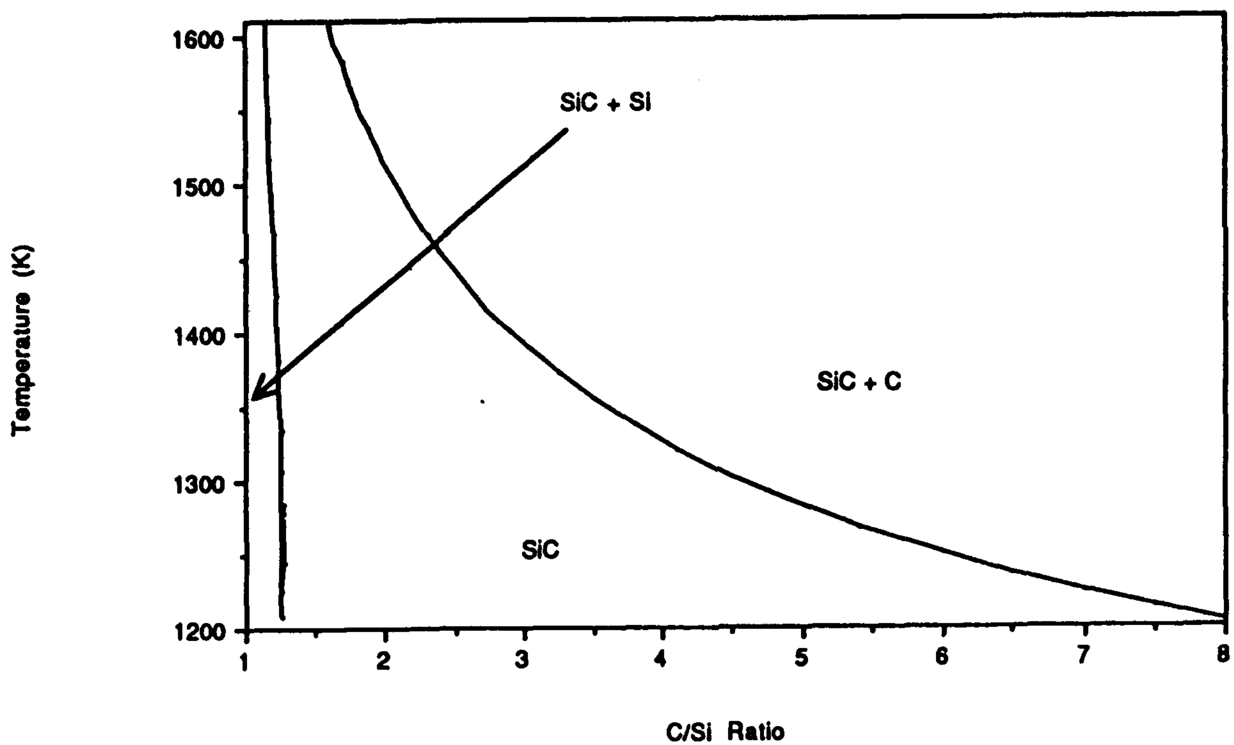


Substrate Coverage:
Silicon provided only through grain boundries



2D Growth:
Continued silicon diffusion through grain boundry results in pitting

Equilibrium Deposition Diagram

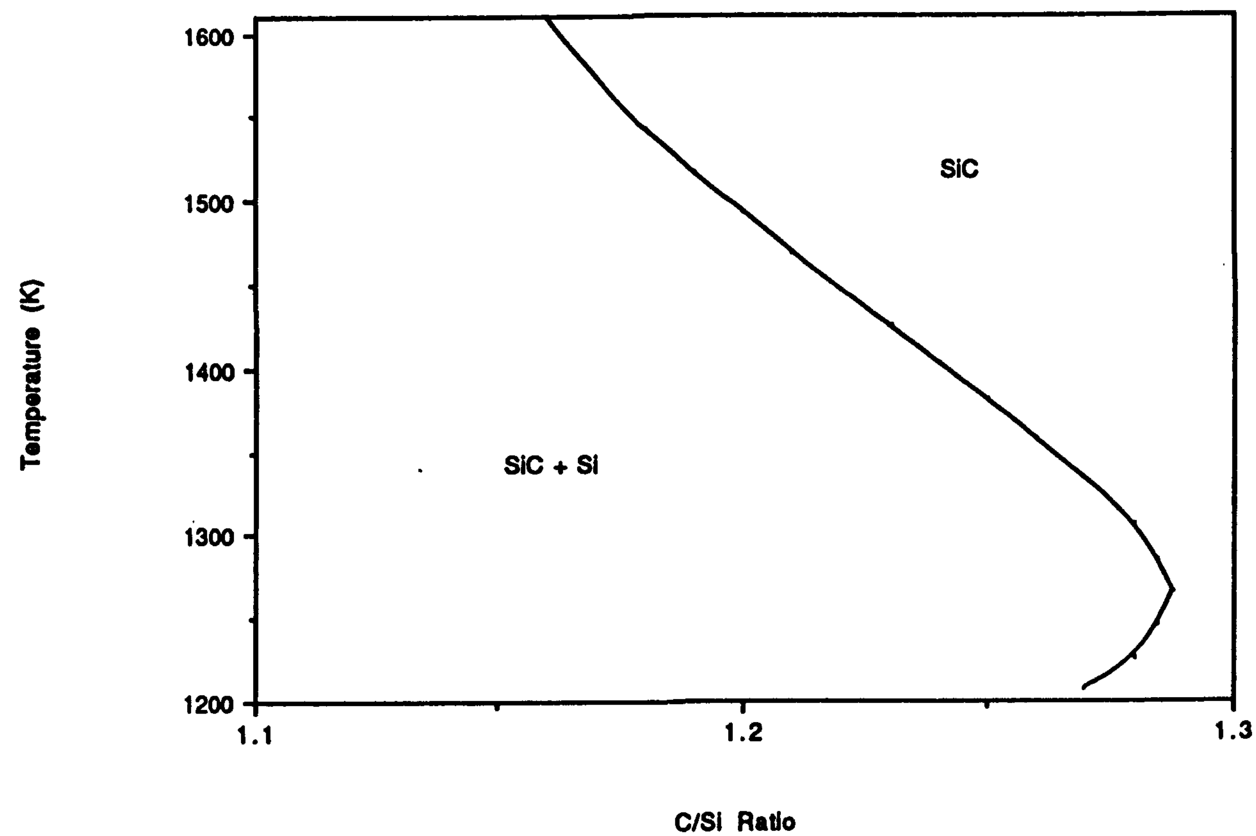


Cl/Si = 4.0

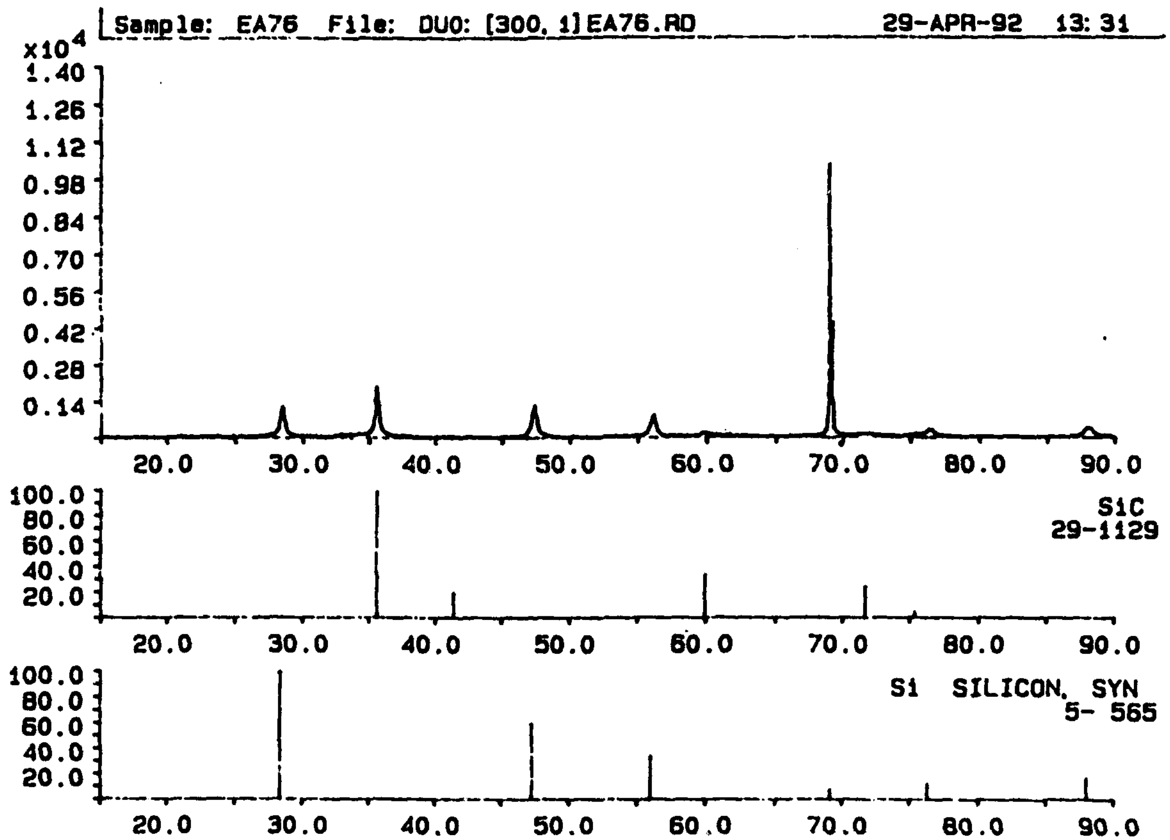
H/Cl = 248

P = 1 atm

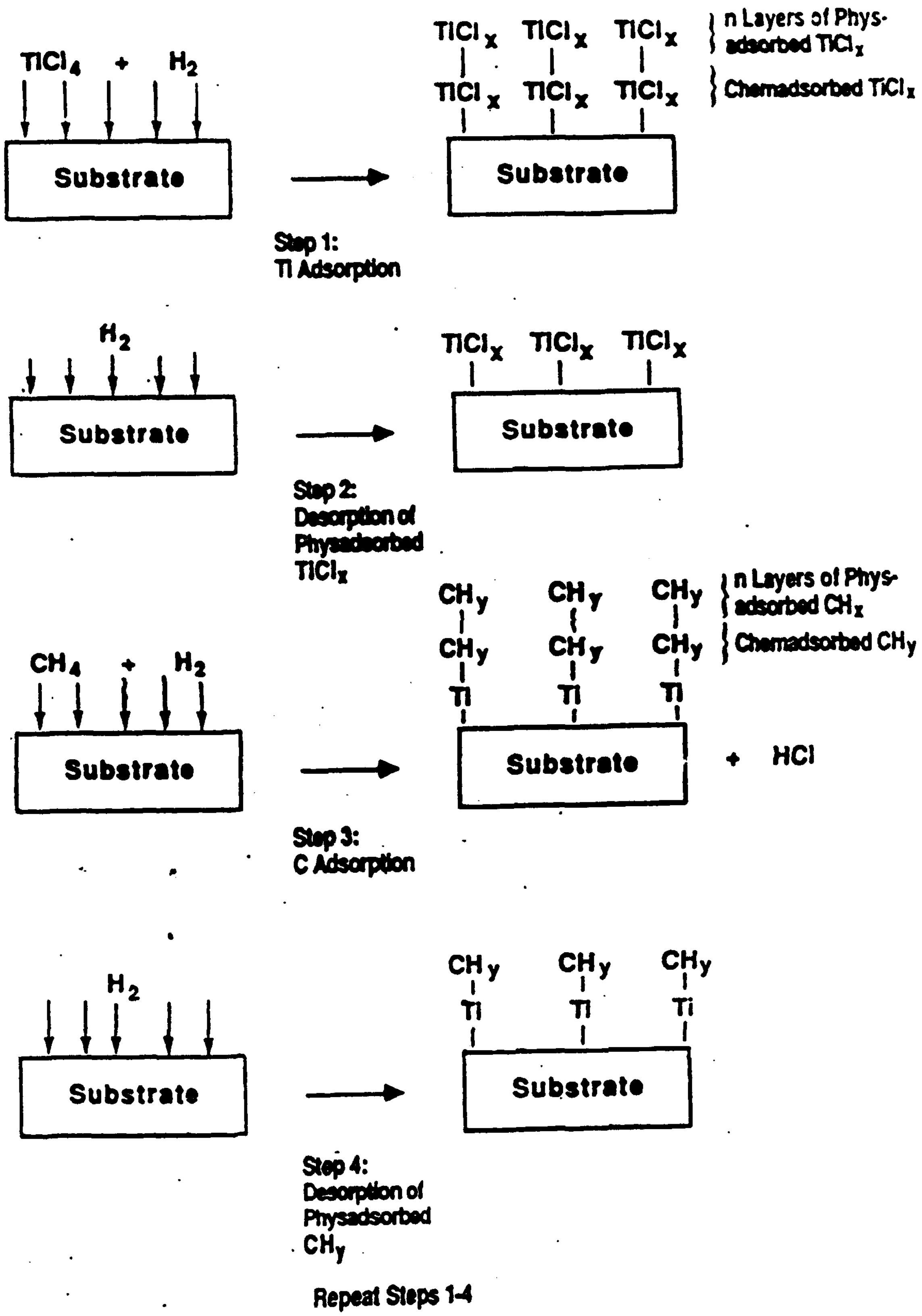
Equilibrium Deposition Diagram



Without Carburization

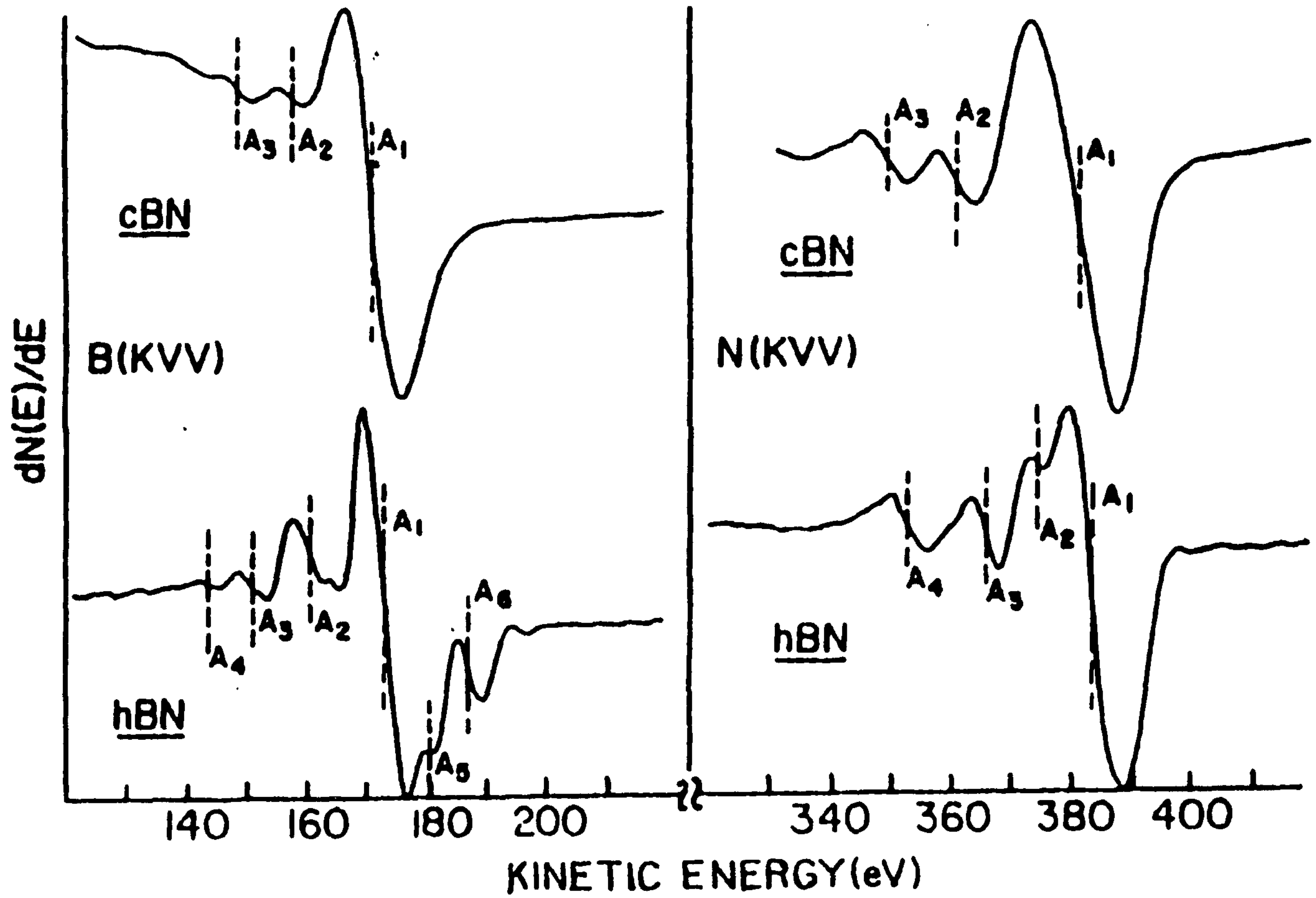


ATOMIC LAYER DEPOSITION (ALD)



Cubic Boron Niride Properties

Hardness:	4.7×10^3
Thermal Conductivity:	10 W/cm
Thermal Expansion:	1.5×10^{-6}
B-N Bond Strength:	152 kcal/mol
Lattice Constant	3.61 Å
	3.57 Å (diamond)

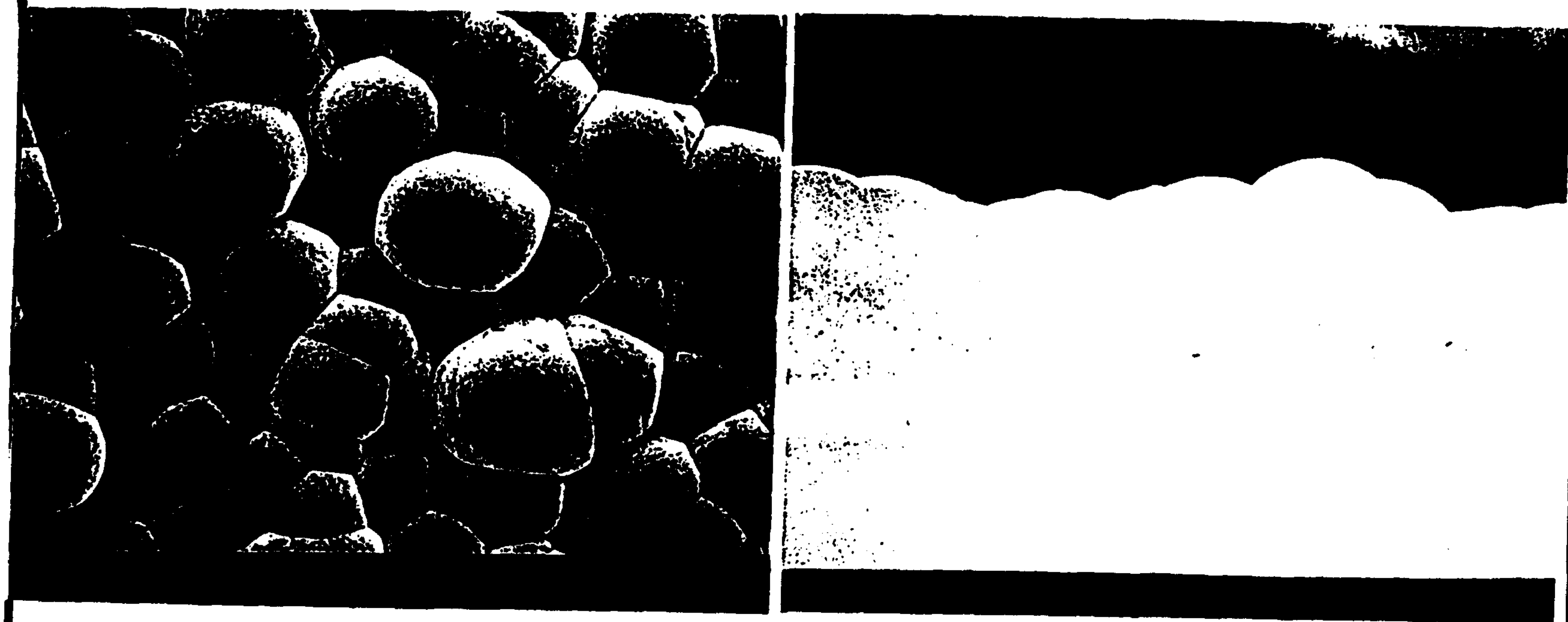


B-KVV and N-KVV Auger spectra of hexagonal and cubic BN.

R. Trehan, Y. Lifshitz, and J.W. Rabalais,
J. Vac. Sci. Technol. A, Vol. 8, No. 6, Nov/Dec 1990

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

CVD BN on Si(100) via BCl_3/NH_3 System



Surface (200 torr, 1000°C) Cross-section

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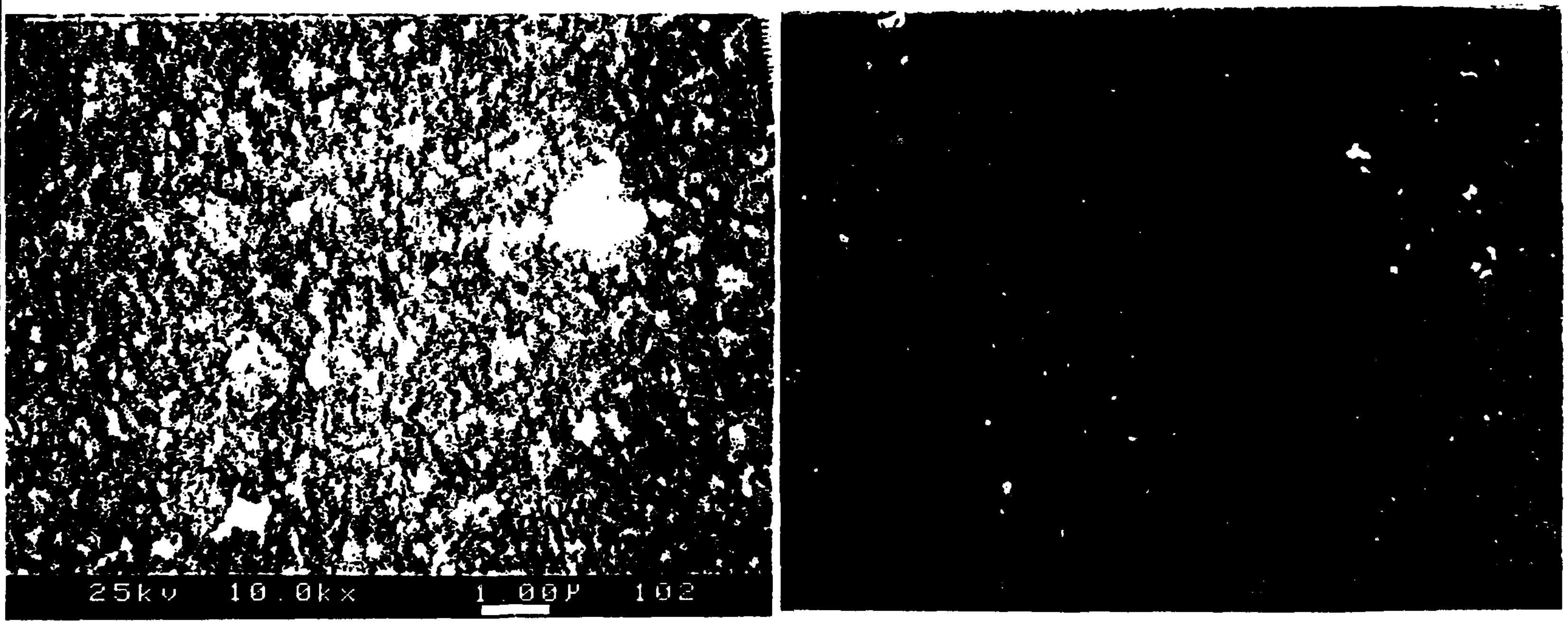
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

CVD BN on Diamond via BCl_3/NH_3 System



Surface (200 torr, 1000°C)

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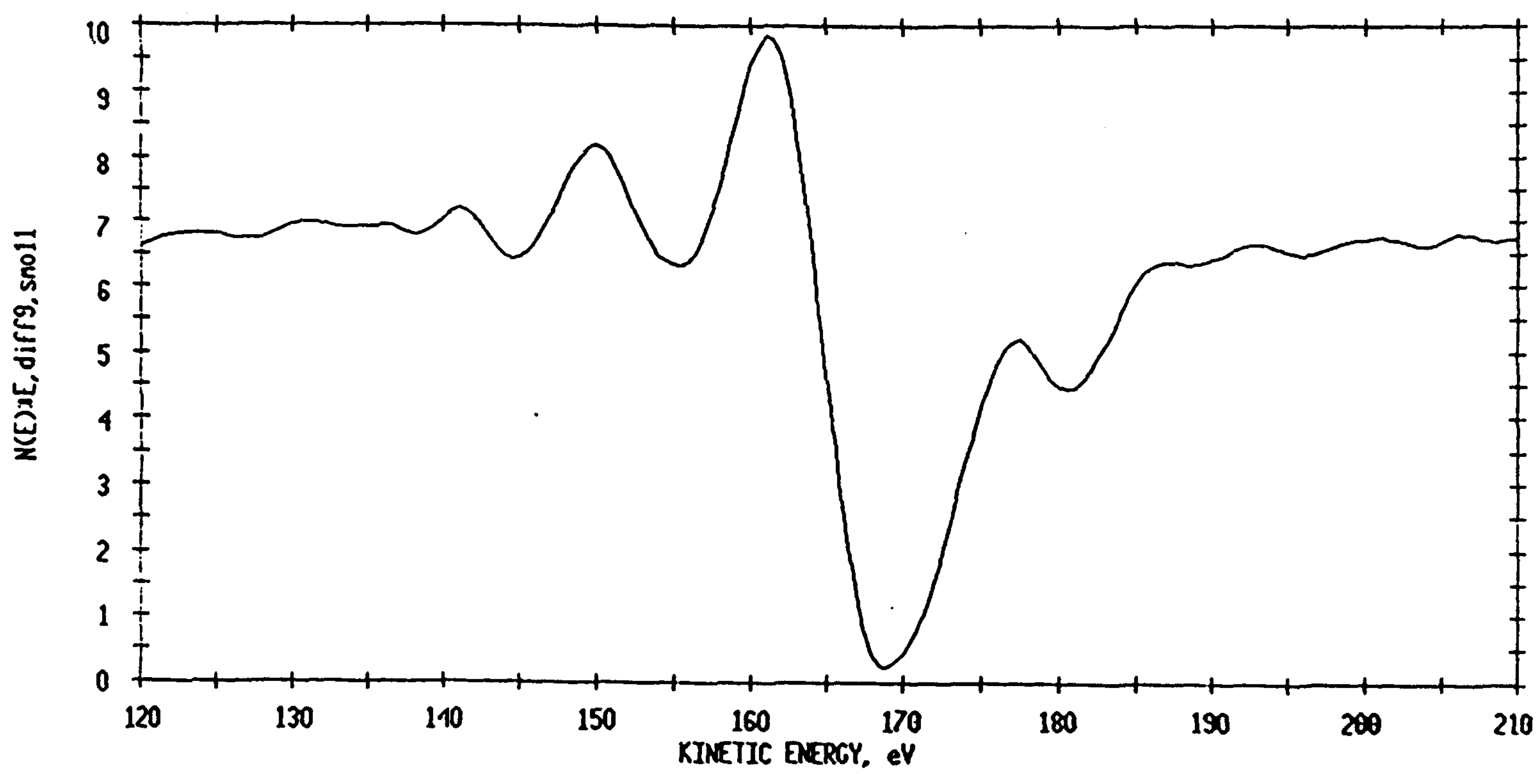
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

B-KVV CVD BN on Diamond(110)



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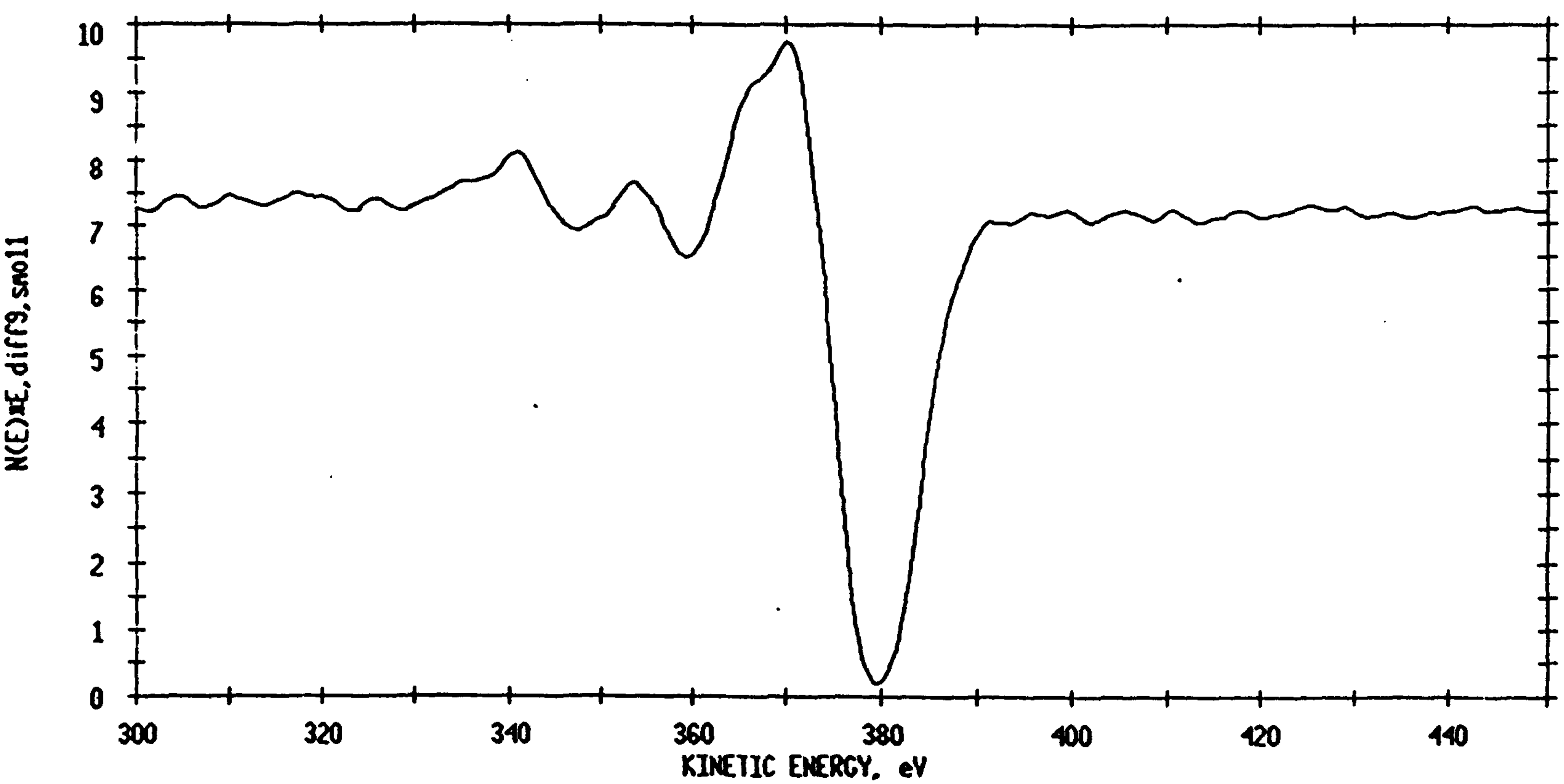
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

N-KVV CVD BN on Diamond(110)



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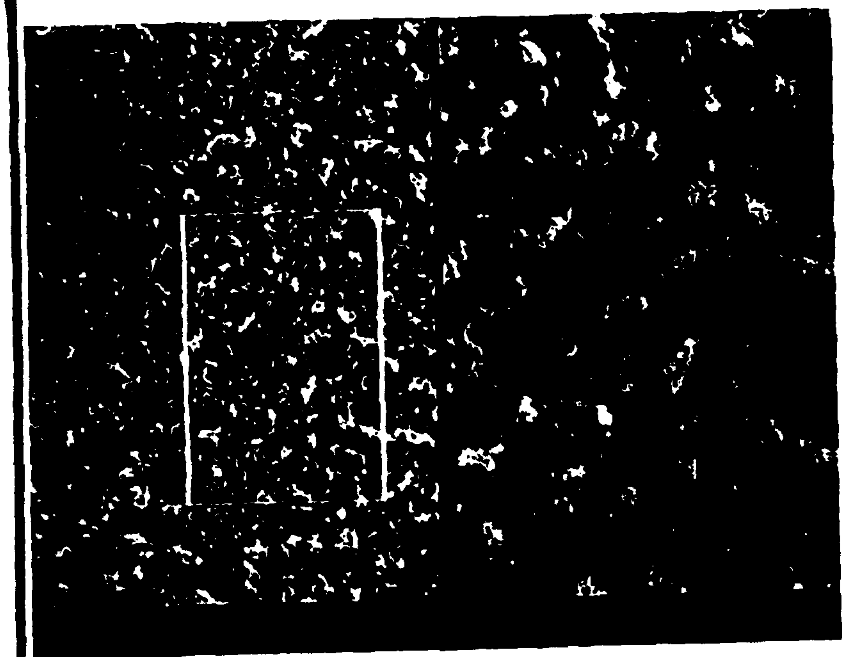
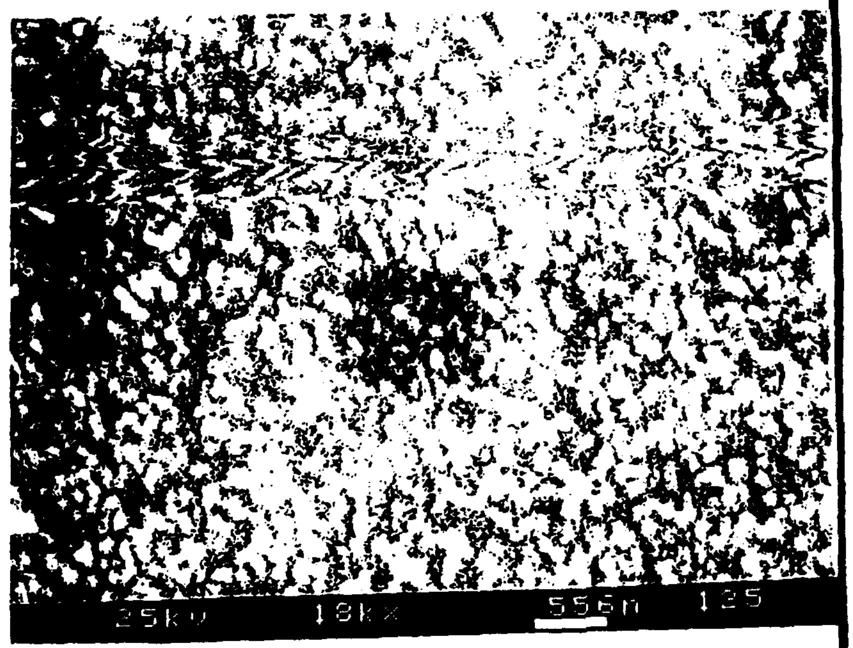
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

ALE BN on Si(100)



ALE BN on Diamond(110)



Surface (200 torr, 1200°C)

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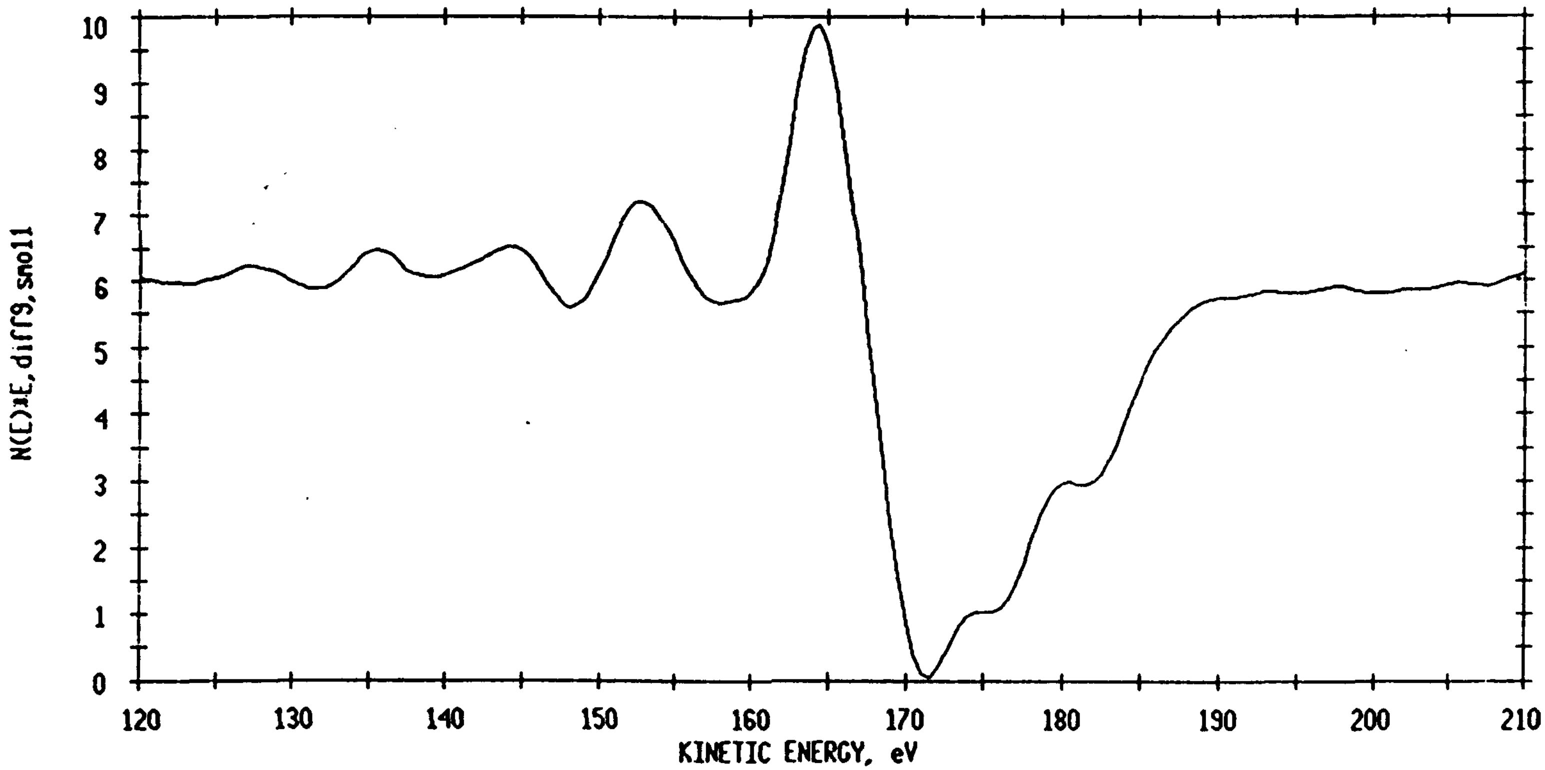
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

B-KVV ALE BN on Diamond(110)



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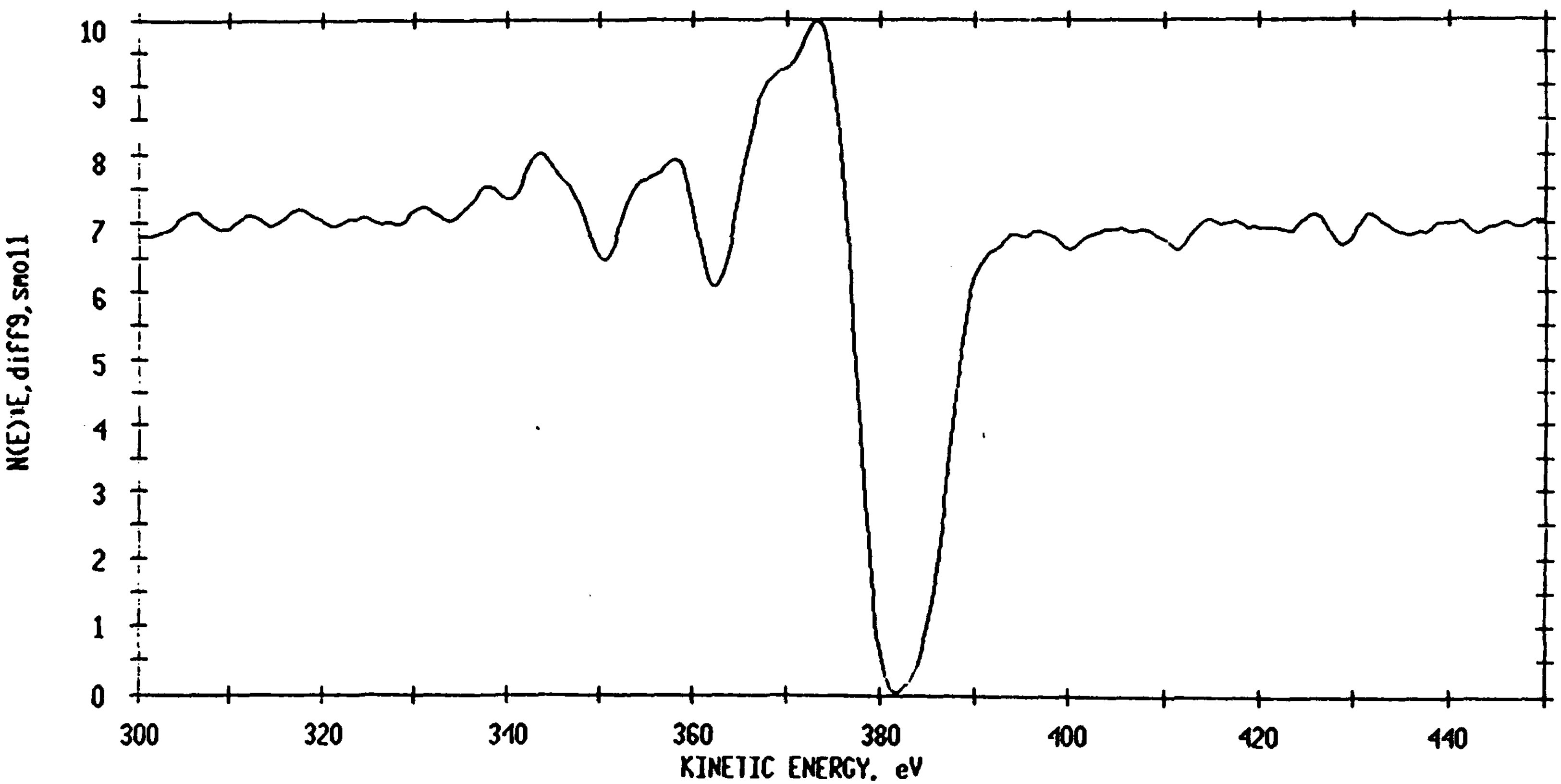
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

N-KVV ALE BN on Diamond(110)



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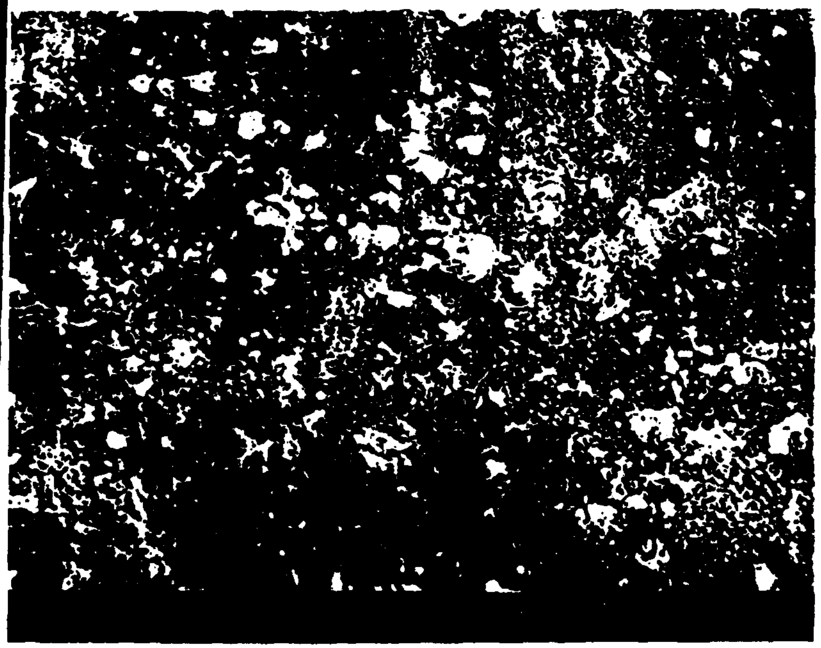
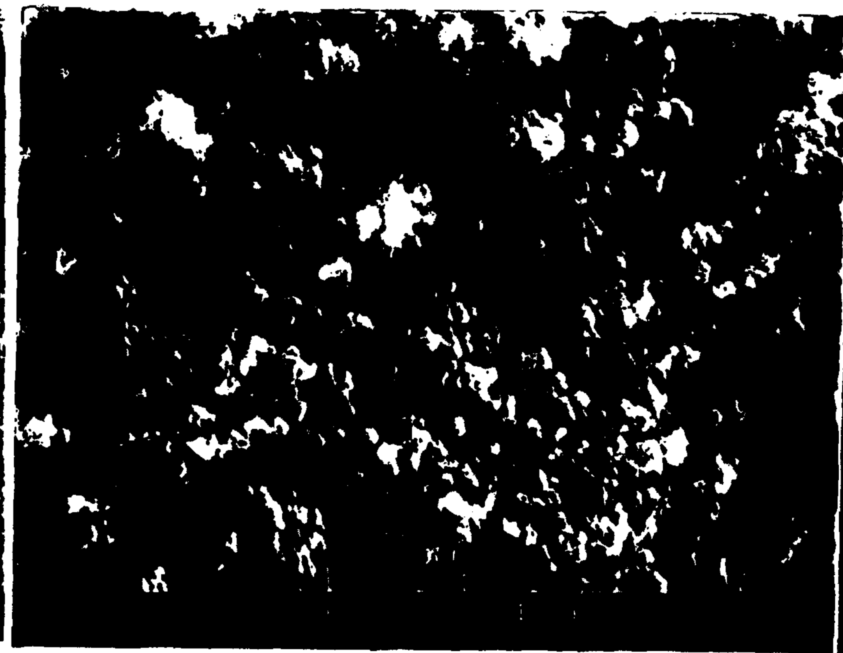
TiN FILM GROWN BY ALE ON Nb





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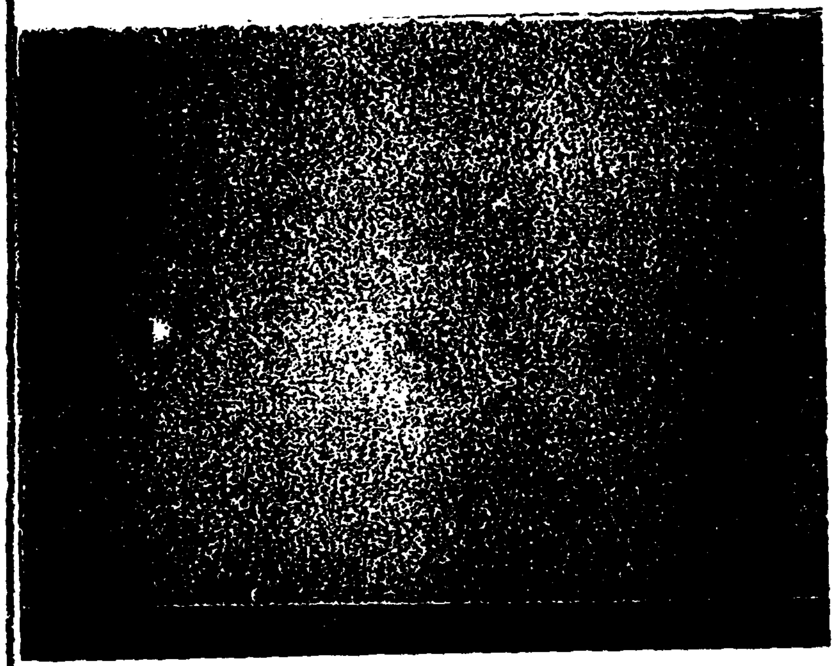
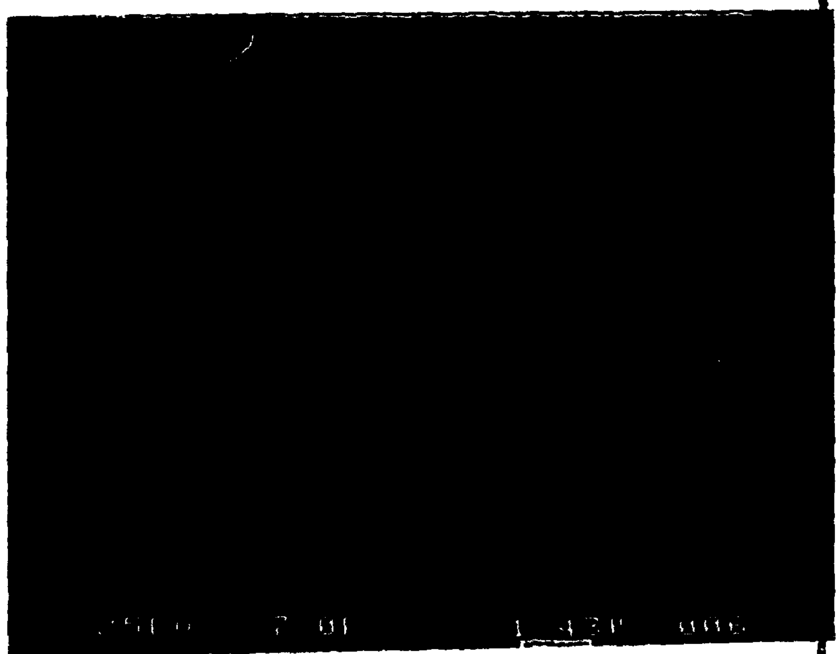
ULTRA-HIGH TEMPERATURE APPLICATIONS

Nb SUBSTRATE PRIOR TO ALE





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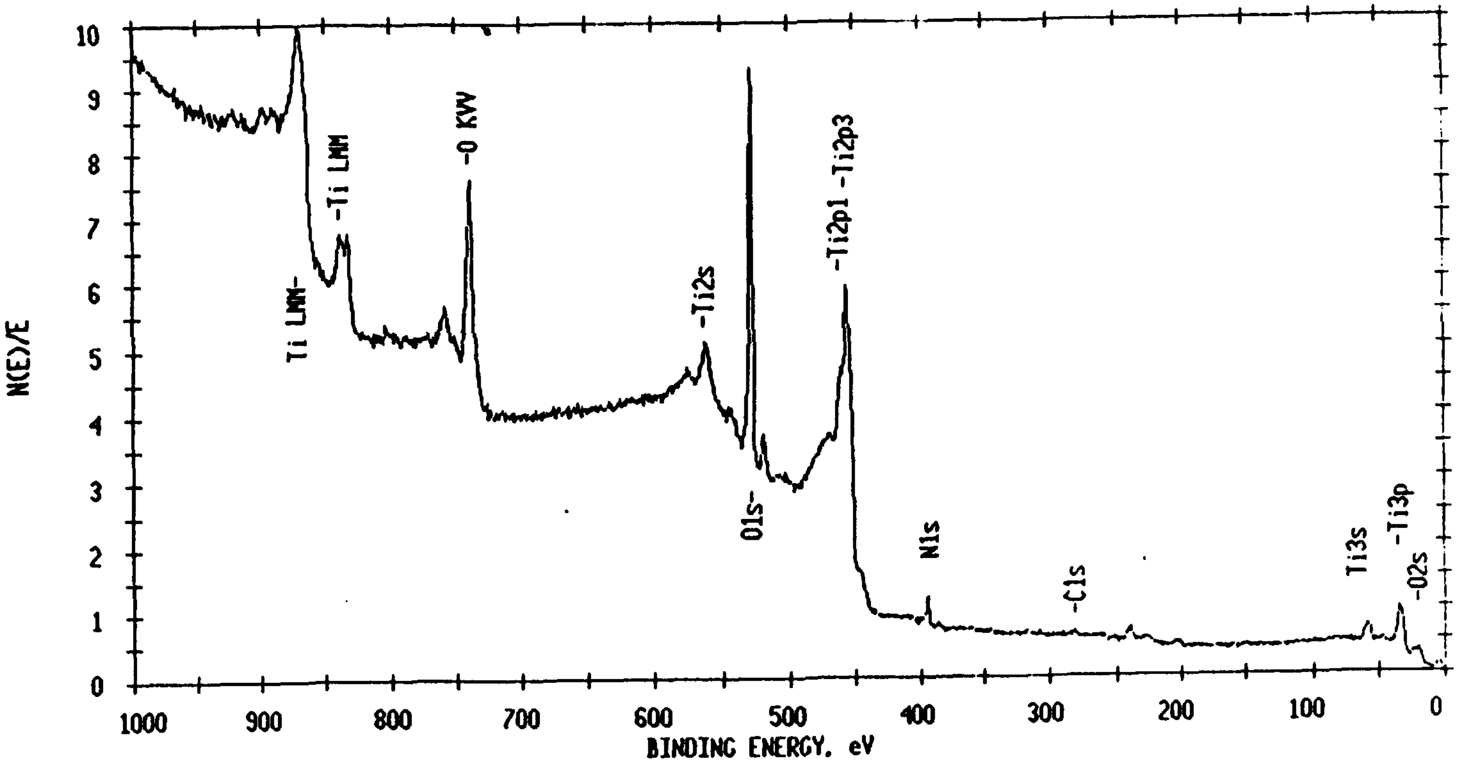
XPS SPECTRA OF TiN FILM GROWN BY ALE



FUTURE PLANS

- Study Novel Chemical Vapor Infiltration Schemes
  - Promise: - Uniform and economical densification of composites with improved mechanical, chemical and thermal properties
  - Applications: CVI of fibrous and powder preforms to fabricate ceramic matrix composites
  - Studies:
    - Optimize HCl injection process for CVI of Nicalon with refractory carbides
    - Process modelling

FUTURE PLANS

- Develop ALD Process
  - Promise: Perfect uniformity, stoichiometry control, interface abruptness
  - Applications:
    - Uniform coatings for surface modification without mass transfer limitations
    - Growth of heterostructures with defined composition and thickness
  - Studies:
    - Understand influence of deposition parameters for various chemistries: TiC, TiN, BN
    - Investigate microstructure, stoichiometry mechanical properties, mixed crystals
    - Investigate new materials: SiC, Tib_2, ZrC, HfC, HfB

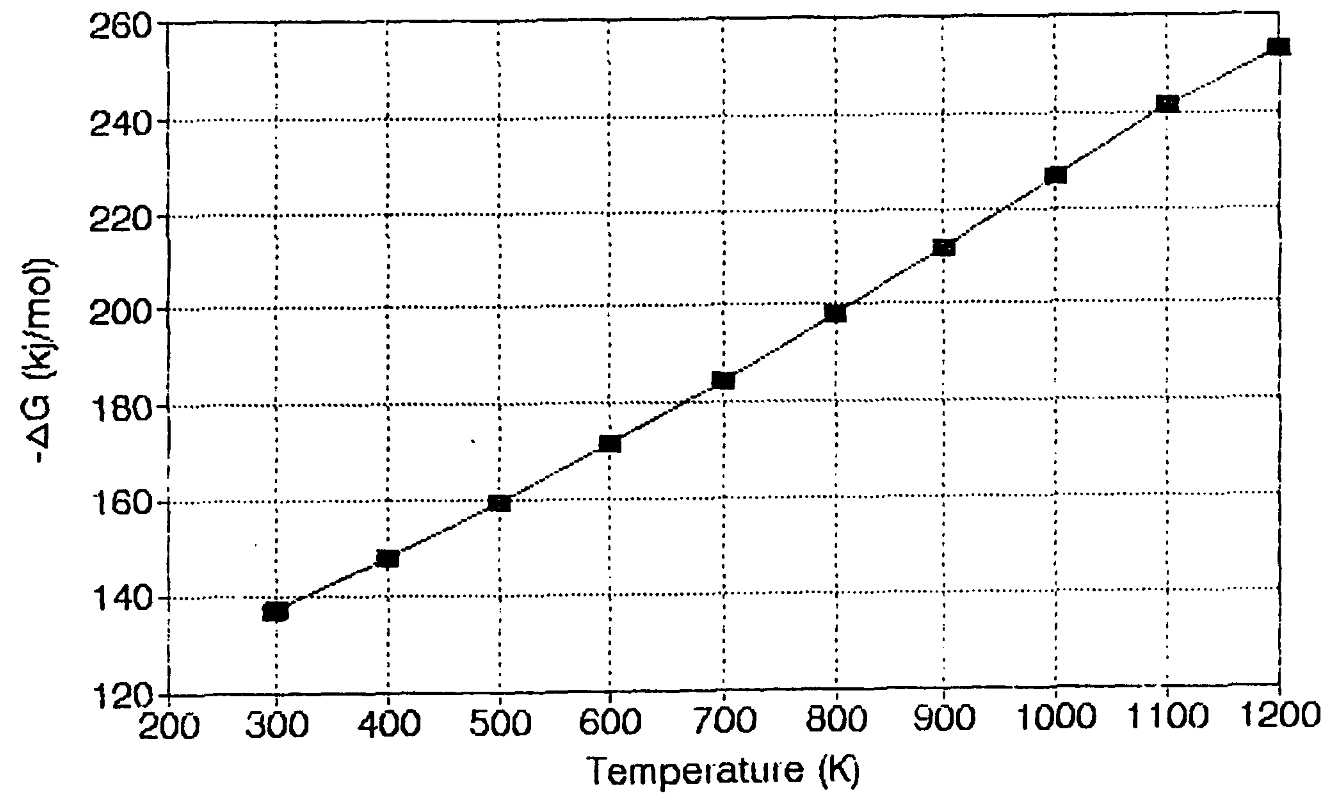
FUTURE PLANS

- Investigate CVD of Cubic BN
  - Promise: Hard, high temperature and stable coating/particle material
  - Studies: N reduction of BP to stabilize the cubic structure

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

ΔG vs Temperature for the Reaction

$BP(s) + NH_3(g) \rightarrow c\text{-}BN(s) + PH_3(g)$



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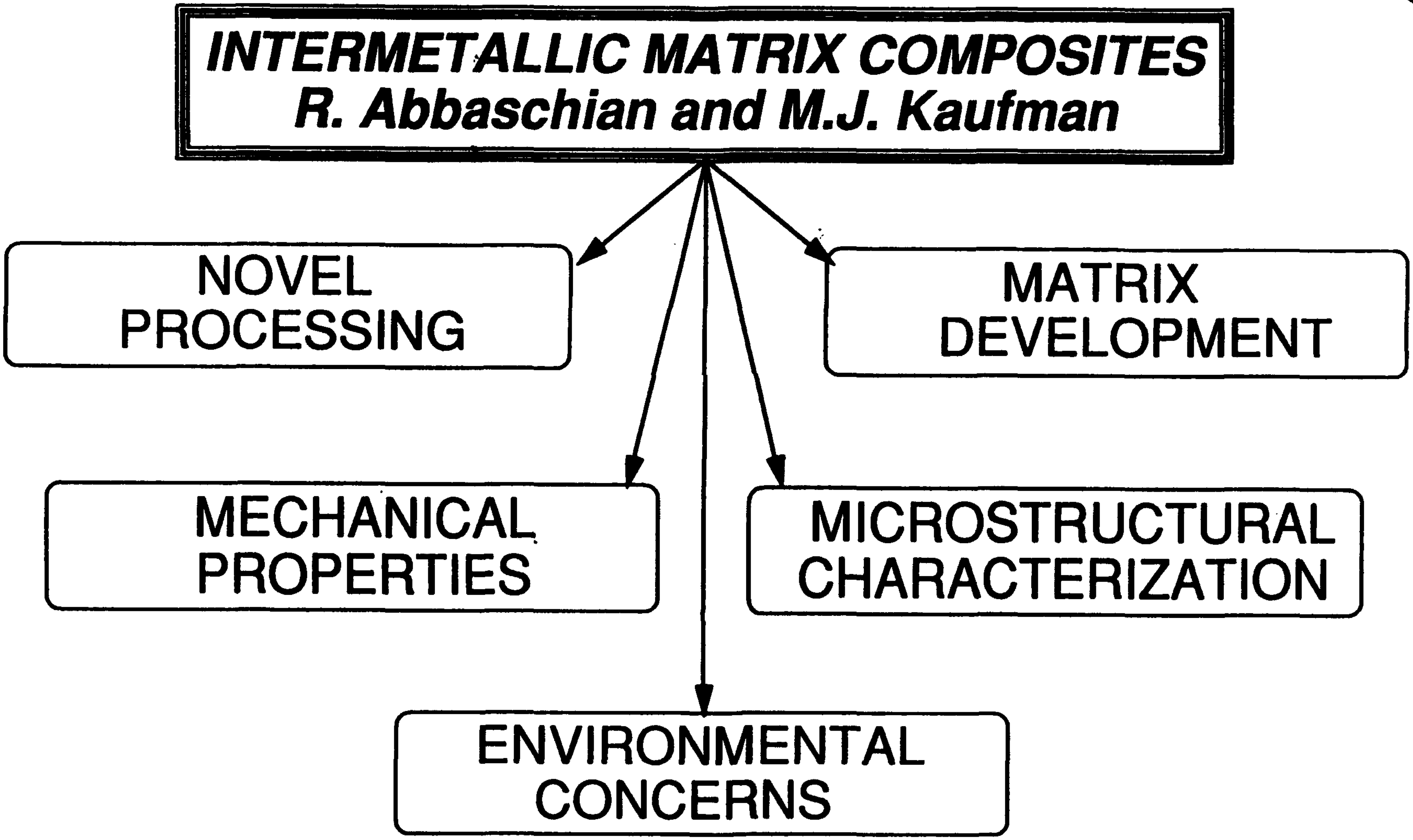
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Personnel

$MoSi_2$

£ L. Xiao - Ductile phase toughening, SiC matrix modification - *TMS Best Graduate Student Paper Award - 1992.*

S. Jayashankar - Silica-free, SiC reinforcements via mechanical alloying

S. Riddle - Ductile phase toughening with mechanically alloyed powders

A. Costa e Silva (ONR) - Interface development & characterization

* Y.S. Kim - Mechanical alloyed vs. commercial purity material, dispersoid effects - *Professor in Korea*

* J.D. Cotton - Powder processing studies - *Los Alamos National Laboratory*

NiAl

H. Doty - Hybrid (niobium + SiC) composites, RHC studies

P. Krishnan (ONR) - Interface development & characterization

$NbAl_3$

* L. Lu - RHC and in-situ alumina coatings in Nb-reinforced composites *Technetics, Inc.*

* A. Gokhale - RHC development & in-situ coating studies - *Post Doc on NASA program*

* R. Erickson - Matrix development in combination with in-situ coating - *Alcoa Technical Center*

$TaTiAl_2$

I. Hwang - Hybrid (Nb + Al_2O_3) composites, in-situ alumina coatings

* M. Weaver - Matrix development & phase equilibria studies - *PhD studies on NASA program*

£ - Recognition ** - Formerly associated with program*

Need for Intermetallics & Intermetallic Matrix Composites

- ***Structural Materials for Next-Generation Aircraft Engines***
  Higher temperature capabilities
  Lower densities (higher thrust-to-weight ratios)
  Environmental stability
  Processability

→ ***Ceramics and Intermetallics***

- *EXAMPLE: Use of NiAl as high pressure turbine blades would reduce the turbine rotor weight (blades and disk) by up to 40% due to lower centrifugal stresses. Also lower tendency for hot spots due to higher thermal conductivity. (Source -- R. Darolia, et al. @ GE)*

*Characteristics of NiAl**

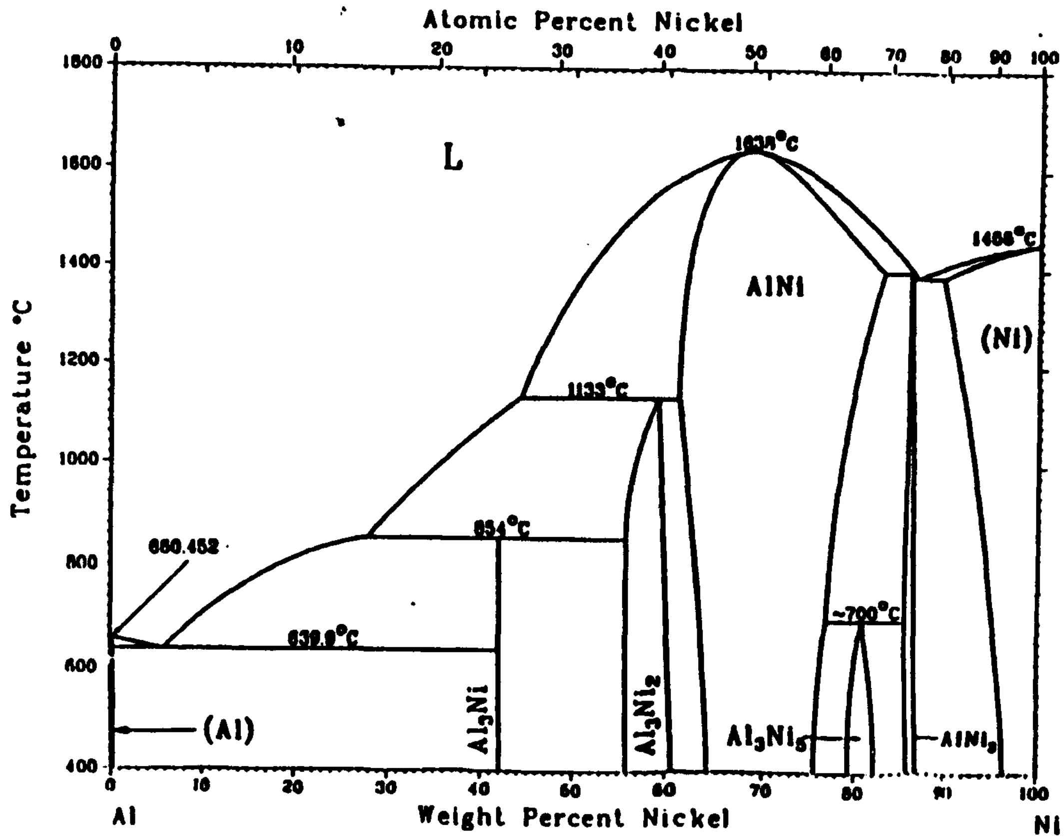
Advantates

- Density ~2/3 that of state-of-the-art nickel base superalloys
- Thermal conductivity 4 - 8X that of nickel base superalloys
- Excellent oxidation resistance
- Simple ordered bcc-like (CsCl) structure
- Lower ductile-to-brittle transition temperature (DBTT) than many other intermetallic compounds
- Higher melting temperature (~300°C) than current superalloys
- Wider solubility range than many other compounds ($MoSi_2$, $NbAl_3$)

Disadvantages

- Low ductility and fracture toughness below DBTT
- Low strength at temperatures above the DBTT

**Source: Darolia, et al. at GE Aircraft Engine Division*



Atomic Percent Nickel
Temperature °C
Weight Percent Nickel
L
1638°C
1455°C
1133°C
854°C
660.452
639.9°C
~700°C
AlNi
(Ni)
(Al)
Al_3Ni
Al_3Ni_2
Al_3Ni_5
$AlNi_3$
Al
Ni

Approaches for Enhancing the Mechanical Properties of Brittle Intermetallics

Low Temperature Properties
- Increase # of active deformation mechanisms by alloying/processing.
- Introduce second phases by alloying or compositing.

High Temperature Properties
- Increase strength by appropriate alloying and processing.
- Introduce second phases by alloying or compositing.

Problem
- Difficult to enhance both low and high temperature properties of a particular compound by alloying/processing.

Possible Solutions
- Use alloying/processing to effect one property and artificially composite to effect the other.
- Use hybrid composite approaches.

Objectives and Strategy

Overall Objectives

Synthesize intermetallic matrix composites with high fracture toughnesses at ambient temperatures and high strength and creep resistance at elevated temperatures.

Strategy

Use ductile refractory filaments to improve room temperature fracture toughness and ceramic fibers or matrix modification to improve the high temperature properties.

Where possible, select reinforcements which are compatible both chemically and mechanically (similar CTE's). If not available, use appropriate interface coatings as diffusion barriers or compliant layers.

Explore novel processing routes to improve microstructural and compositional control, increase process efficiency, minimize contamination, and control reinforcement alignment.

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Areas of Focus

- **Novel Processing:**
  Reactive Hot Compaction
  In-situ Displacement Reactions
  In-situ Coatings
  Other Coating Schemes (sol-gel, PVD, CVD)
  Multiple Reinforcements

- **Matrix Development:**
  Alloying Effects
  Phase Equilibria and Transformations
  Microstructural Evolution
  Thermal Stability
  Second Phase Toughening
  Deformation Characteristics

- **Characterization:**
  Mechanical Properties (vs. Temperature)
  Structure/Property Relationships
  Environmental Effects

Reactive Hot Compaction

Impetus

- Simple application of temperature + pressure
- Uses transient liquid phase -- easier densification
- High density compacts are easily achieved
- Lower processing temperatures required - less fiber degradation)
- Can control reaction rates to some extent
- Can combine with in-situ compositing schemes
- Cost effective

Important Parameters

- Temperature, pressure and time
- Heating rate
- Initial stoichiometry and powder size(s) and distribution (mixing)
- % elemental vs. prealloyed powders (for reaction control)

RHC of Aluminides

- Intermetallic formed from elemental powders
- Highly exothermic reaction
- Slow controlled heating → Al melts first
- Reaction rate depends on rate at which ΔH_{form} can be dissipated
- Application of pressure fills pores
- Time at T & P to densify and homogenize

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

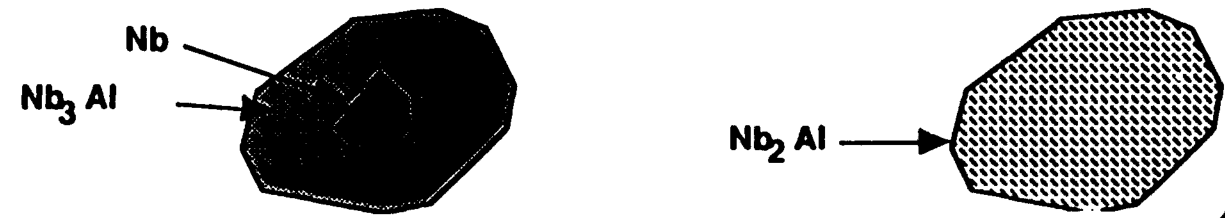
(1) Mix Nb and Al Powders in desired stoichiometry
(2) Produce green compact
(3) Hot press in BN lined graphite die
(4) During hot pressing, apply pressure during reaction propagation (~ after 15 min at 1350°C)

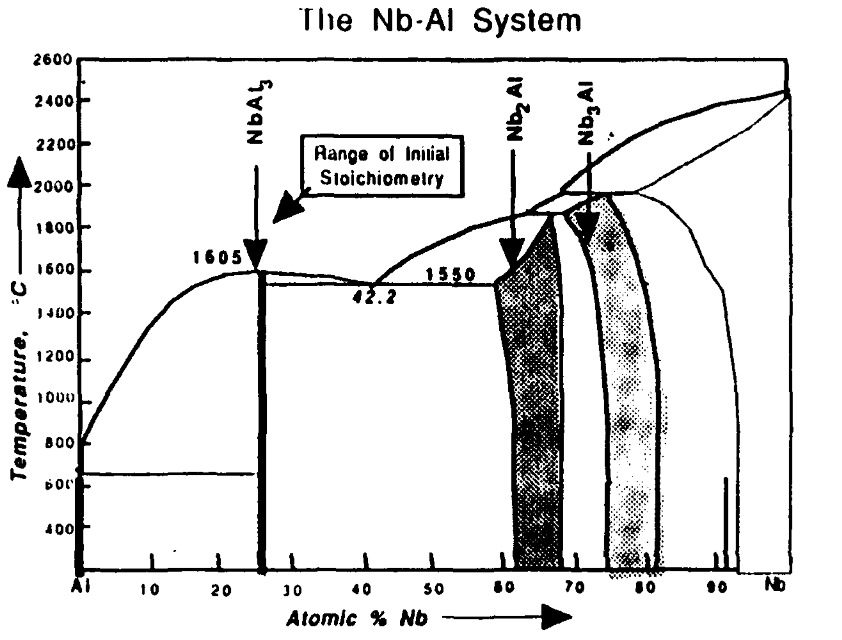
RHC Processing Sequence

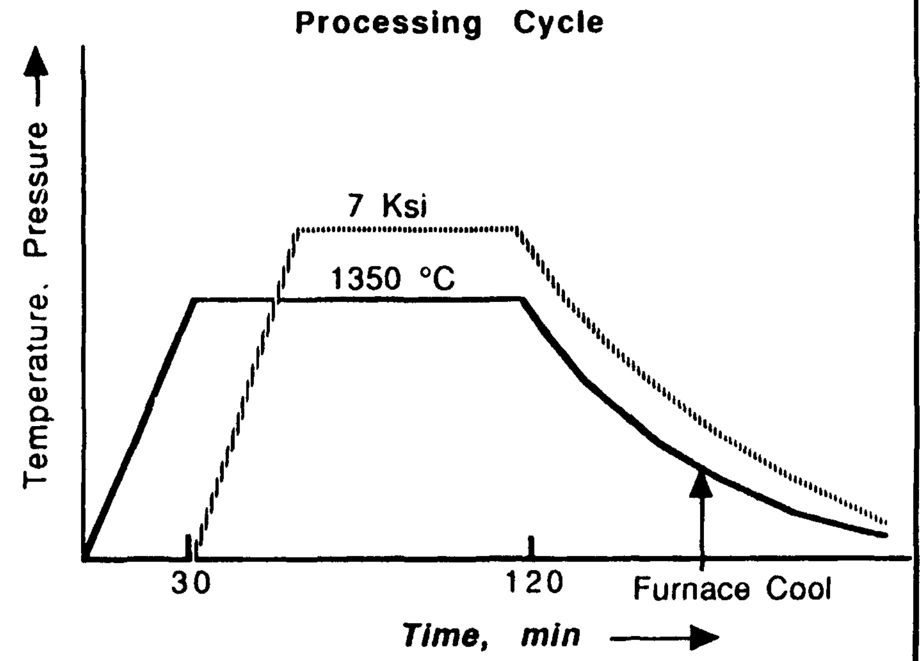
Effect of Powder Particle Size on the Composition of Second (or multi) phase particles

Nb < 44 μm
Al 20 μm
(average)

Nb < 37 μm
Al 6 μm
(average)

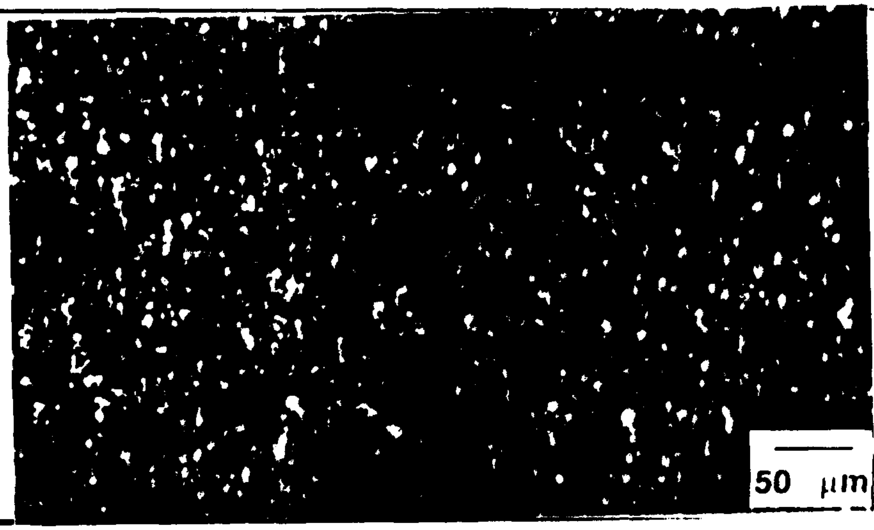


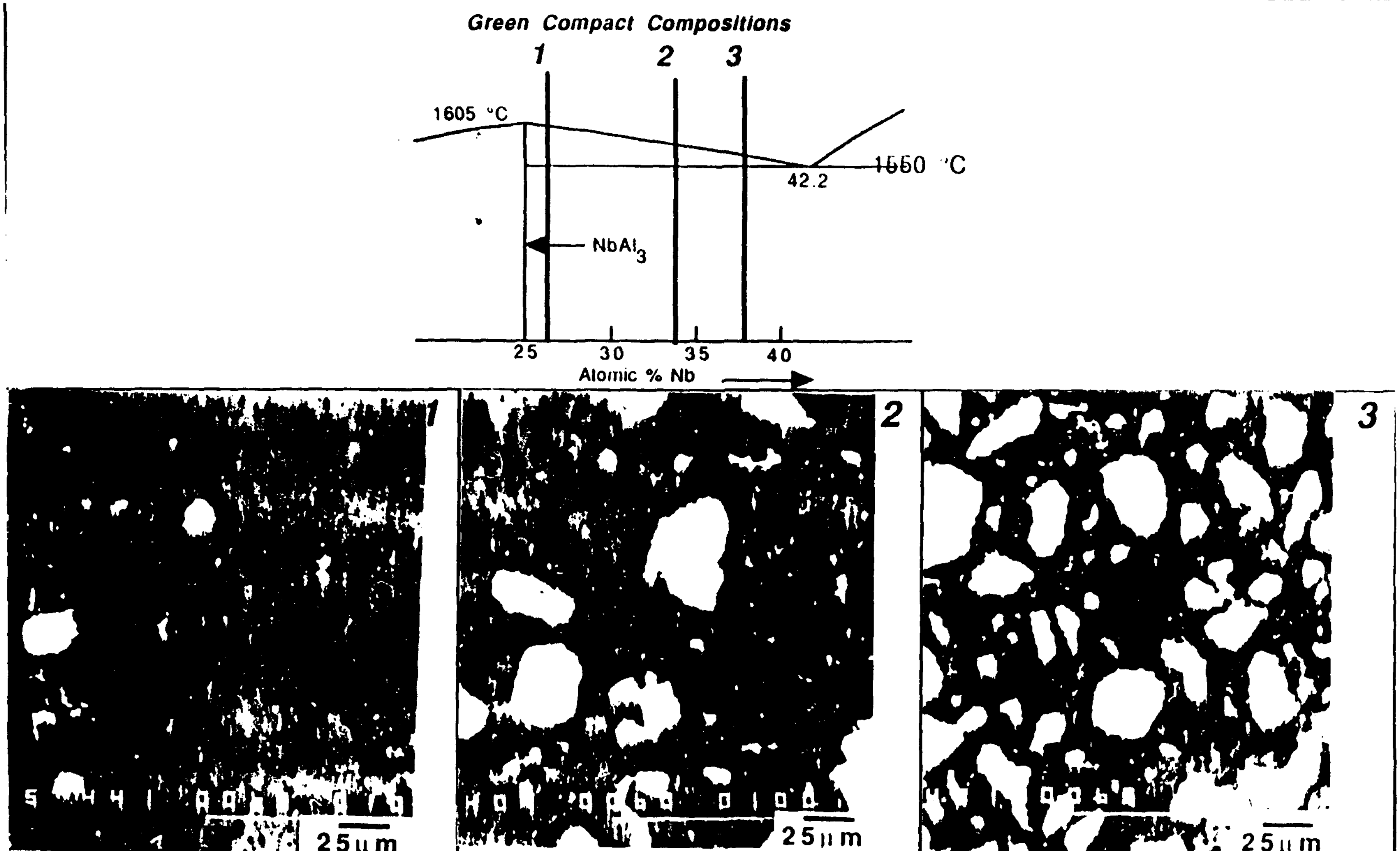




RHC Processed $NbAl_3$

Volume Fraction
of Porosity < 2%

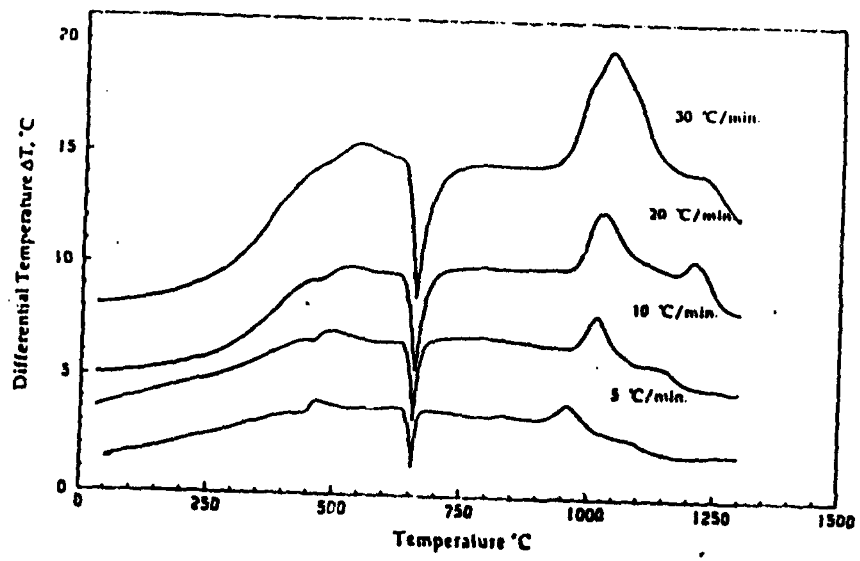




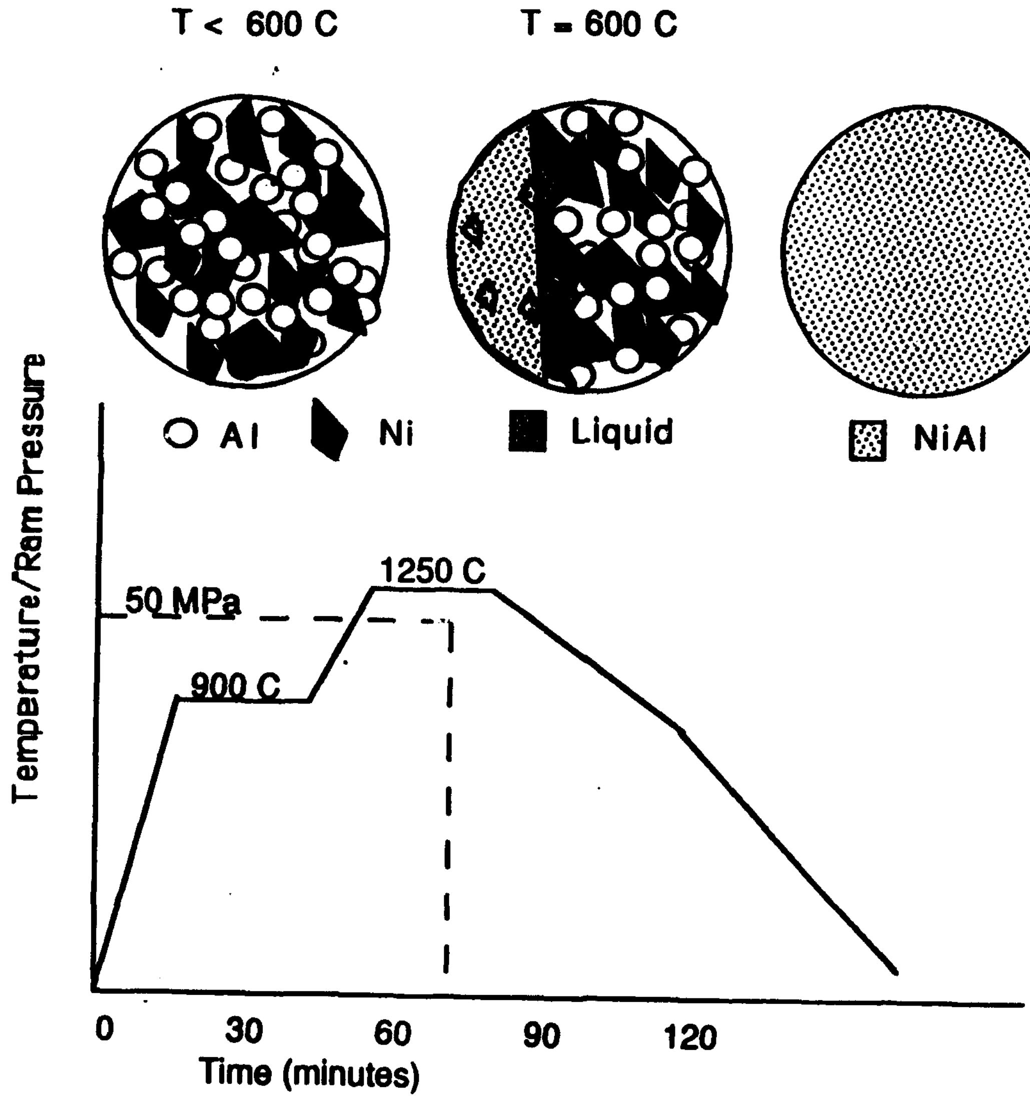
Volume Fraction 6.9%	Volume Fraction 14.6%	Volume Fraction 27.68%
Mean Spacing 383.8 μm	Mean Spacing 142.4 μm	Mean Spacing 75.1 μm

Effect of Heating Rate

DTA profile of Nb and Al powder samples ($NbAl_3$ composition) performed at four heating rates



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



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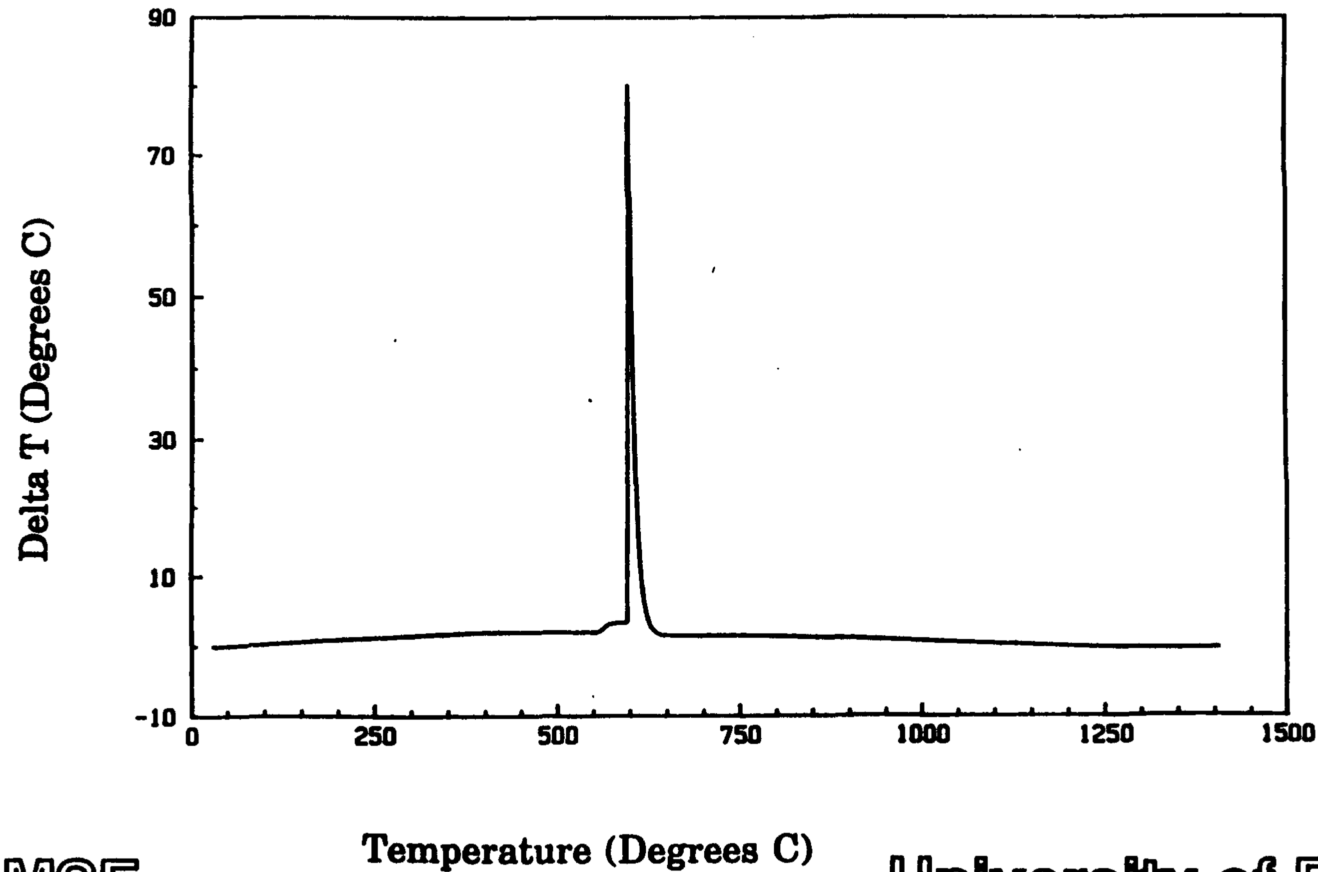
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Differential Thermal Analysis
Sample : NiAl
Reference : Al2O3 CR75
Heating Rate : 10 Degrees C per minute
Atmosphere : Argon
Peak Delta T = 87 at 590 Degrees C



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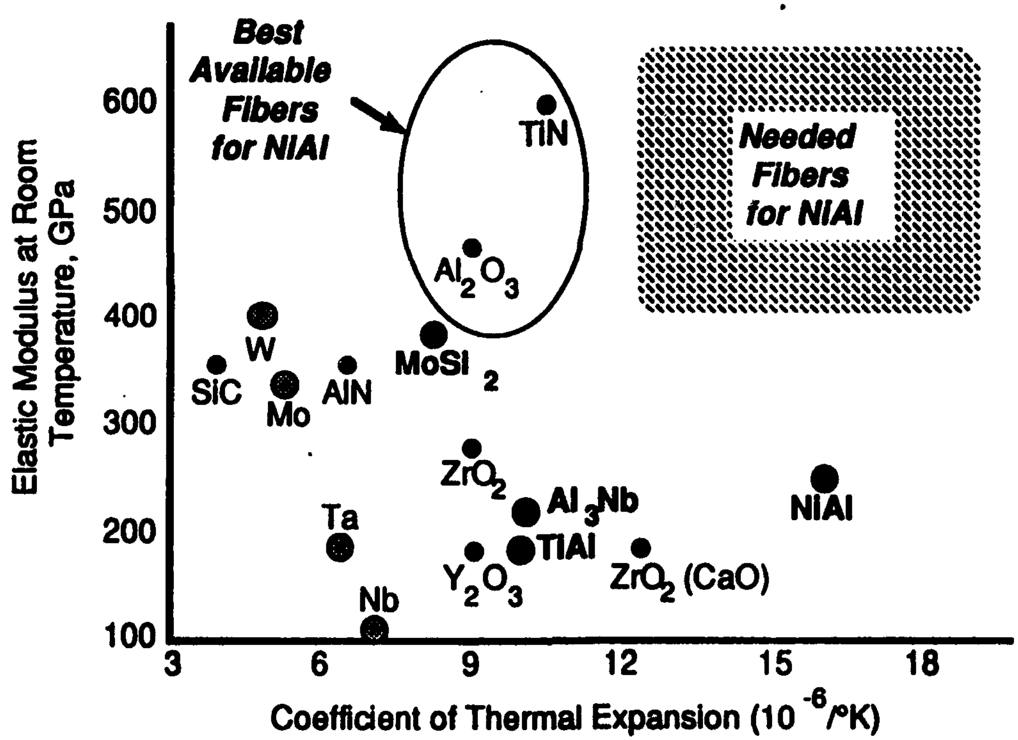
Matrix-Reinforcement Considerations

- **Mechanical Properties of Matrix and Potential Reinforcements**
- **Microstructural Stability (Anticipated Reactions)**
- **Mechanical Stability (CTE & Modulus Mismatch)**
- **Interface Properties (Weak vs. Strong; Nature of Bonding)**
- **Effect of Reinforcement on Environmental Stability (e.g., Refractory Metal Toughening)**

Note: For most matrix/reinforcement combinations, there are problems with one or more of the above issues and interface modifications are required!! Unfortunately, it is difficult to solve all problems with a single interface.

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Fiber Selection



Impetus for In-Situ Reactions

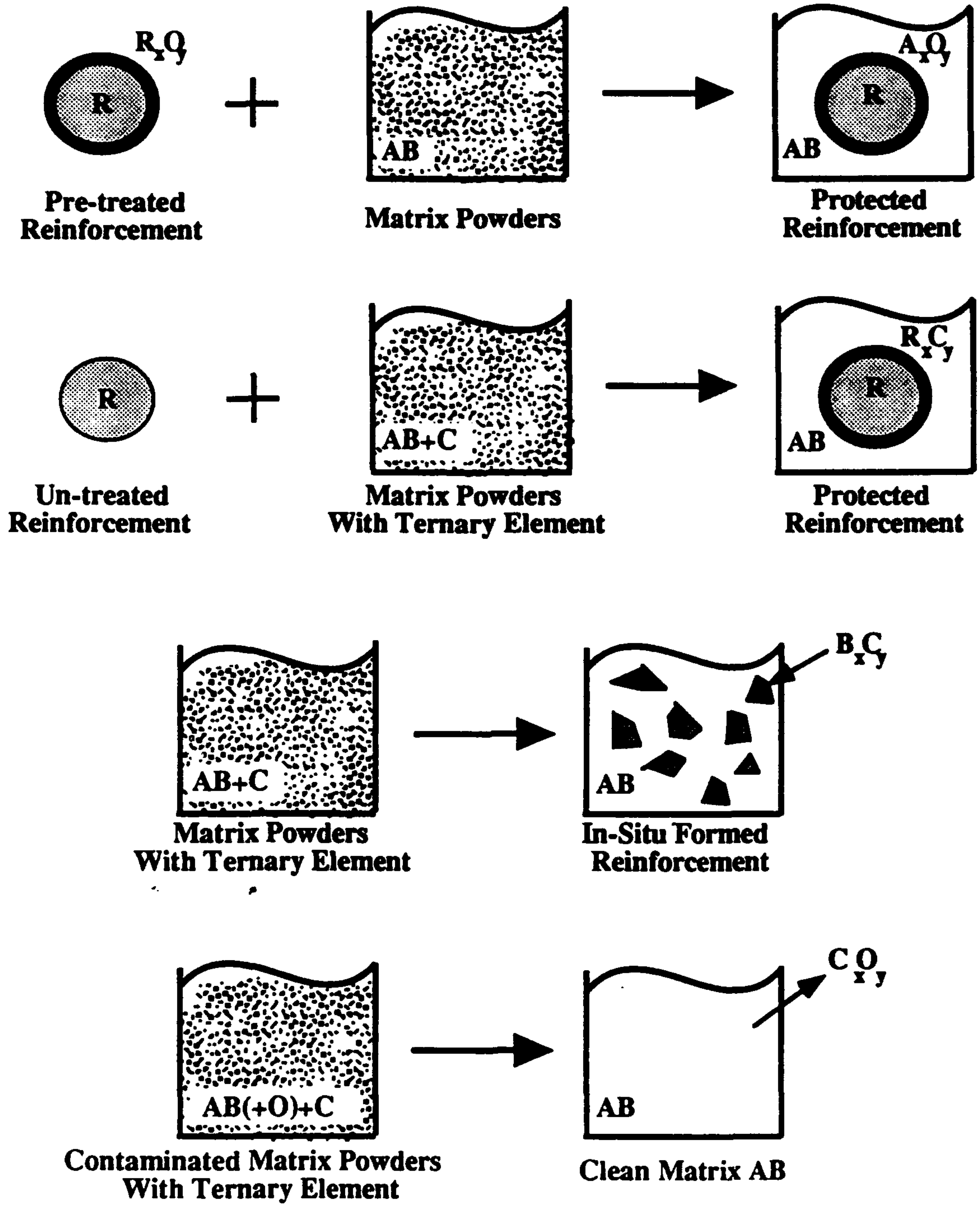
- Traditional coating schemes (sol-gel, CVD, PVD, etc.) tend to be expensive and unreliable.
- Need for simple, reliable processing schemes that are cost effective.
- In-situ reactions offer numerous advantages over traditional schemes.

    1. Form dispersoid or reinforcements in-situ with uniform distributions.

    2. Form uniform interface coatings readily in some systems.

    3. Product phases are usually more compatible from a thermodynamics standpoint.

Typical Reaction Scenarios



Combinations of the Above

Application to Intermetallic Matrix Composites

- ***Microstructural Stability***

  Thermodynamic & Kinetic Considerations
  (Diffusion Couples, Equilibrium Calculations)

- ***Mechanical Stability***

  CTE Mismatch Considerations
  (Compliant Layers, Matrix CTE Modification)

- ***Optimum Interface Properties***

  Weak Interface for Toughening
  Strong Interface for Strengthening
  Reliable Measurement Techniques (Push-out, Pull-out, etc.)

$NbAl_3$ Composites

Ductile phase toughening

- RHC studies
- *In-situ* interface coatings
- Mechanical properties

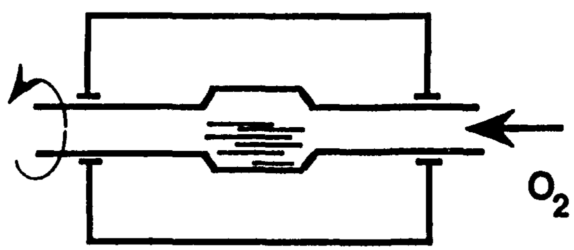
Matrix development

- Alloying to effect the $DO_{22} \rightarrow L1_2$ transformation
- Alloying to enhance slip and/or twinning
- Second phase effects
- Combination of enhanced matrices with *in-situ* coating scheme

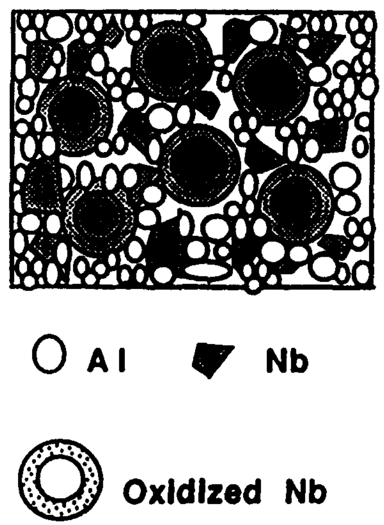
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Proc sing Sequence for Fabrication of In-Situ Alumina Coated Nb/NbAl $_3$ Composites : Coupling of Pre-Oxidation and RHC

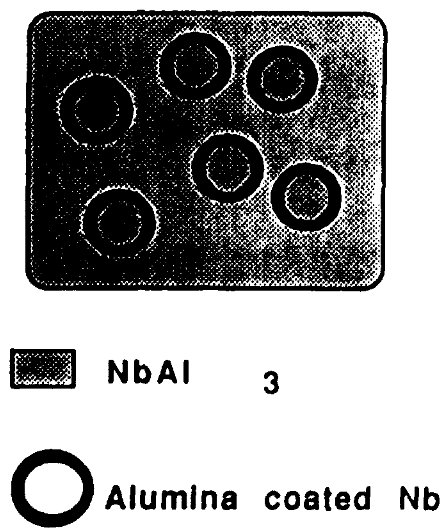
Pre-surface-oxidation of Nb filaments



Green compation of mixture of Nb, Al powder and the oxidized Nb filaments



Final product of in-situ coated Nb/NbAl3 composite



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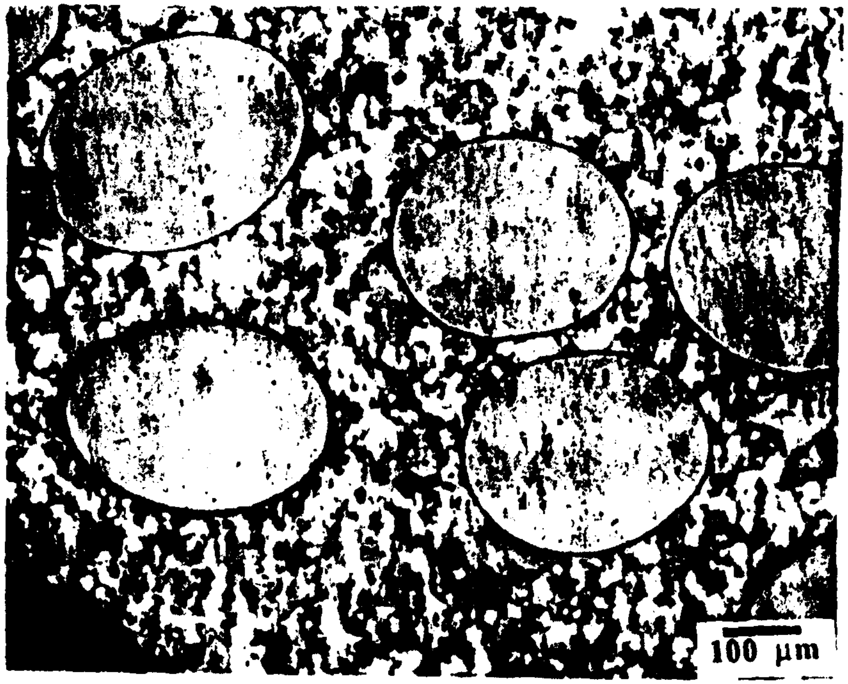
Nb Filaments Without Diffusion Barrier

Absence of Diffusion Barrier Results in Embrittlement of Nb Filaments by Al and an Extensive Interaction Zone

Nb Filaments With Diffusion Barrier



Preoxidized Nb Filaments Produce an "In-Situ" Alumina Diffusion Barrier During RHC. Note the Absence of Nb Embrittlement and Interfacial Reaction Zone

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THERMAL STABILITY AT 1200°C. ANNEALED FOR 100 HOURS

Uncoated Nb Filament

"In-Situ" Coated Nb Filament

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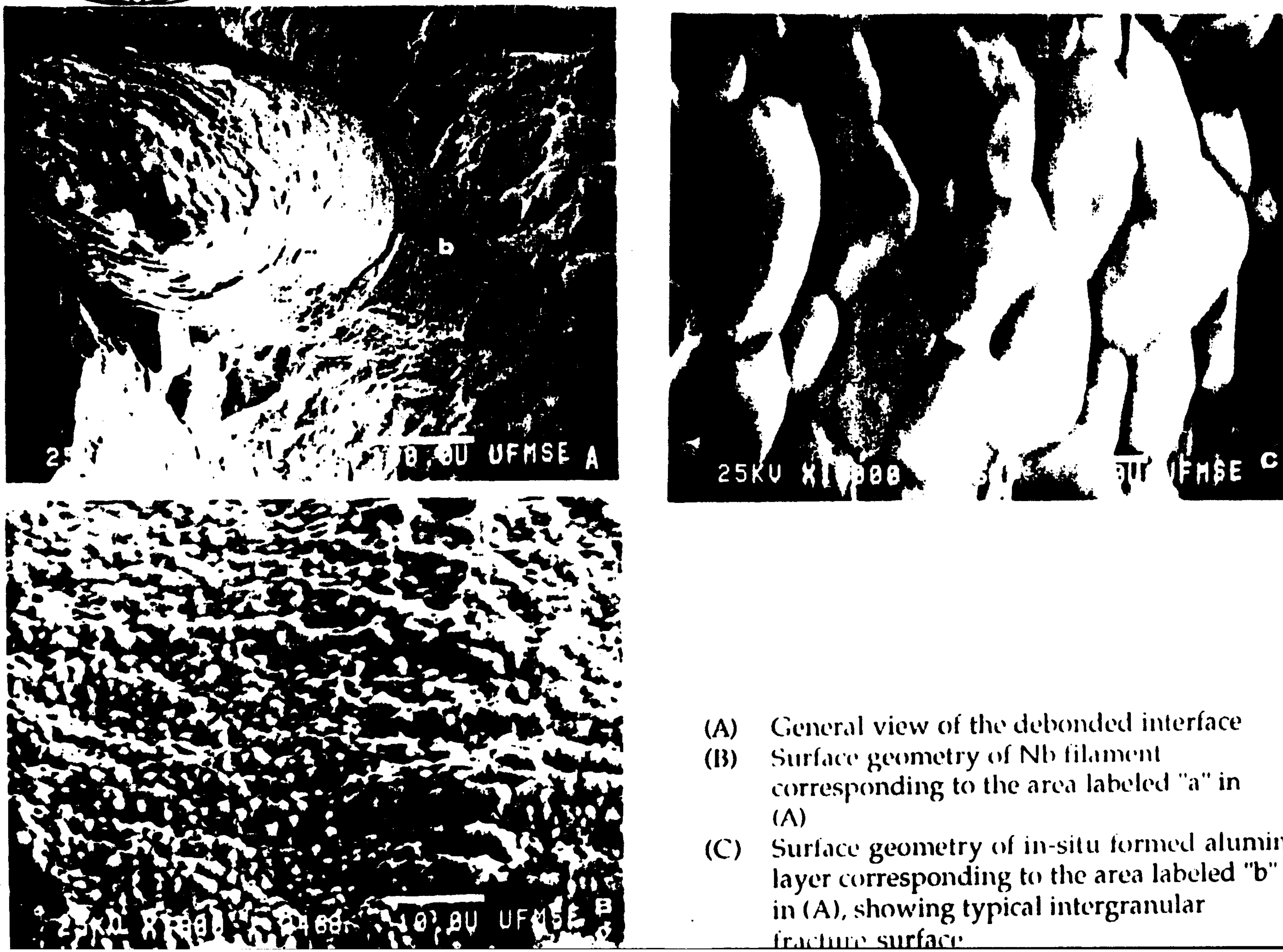
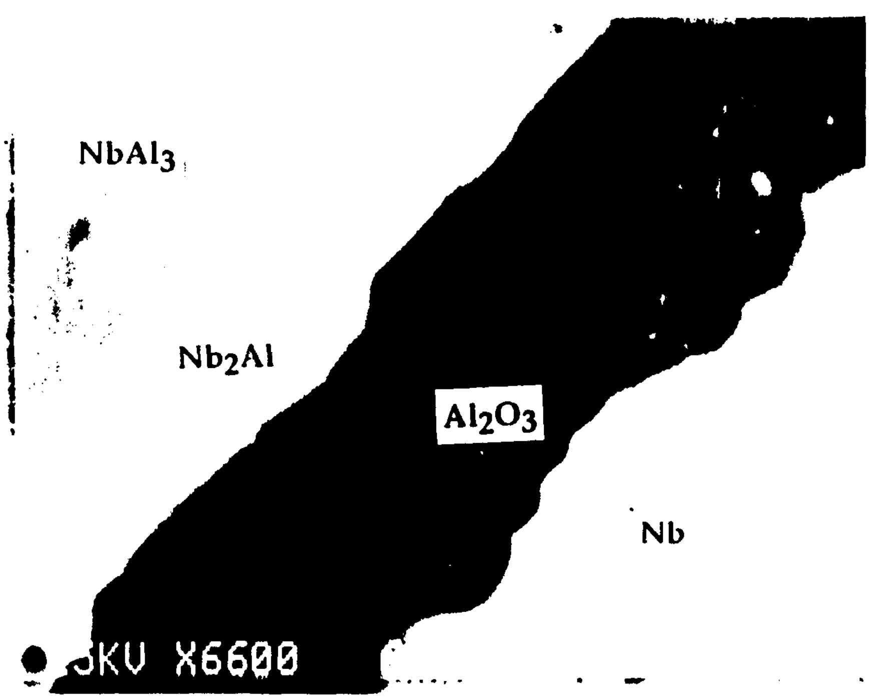


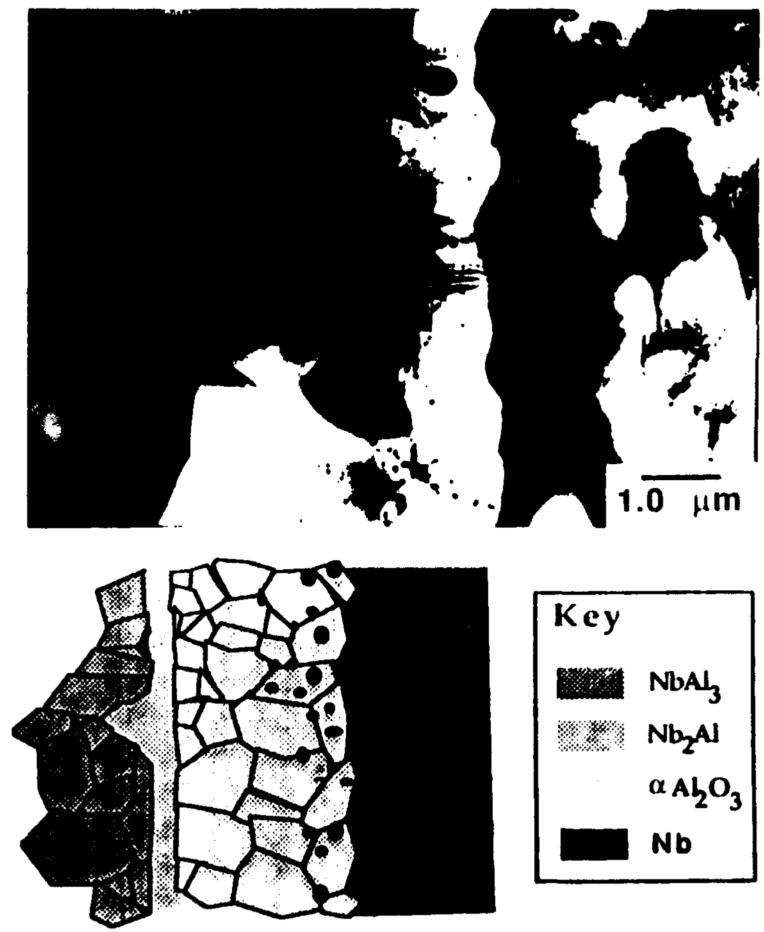
(A) General view of the debonded interface
(B) Surface geometry of Nb filament corresponding to the area labeled "a" in (A)
(C) Surface geometry of in-situ formed alumina layer corresponding to the area labeled "b" in (A), showing typical intergranular fracture surface

Microstructure of In-Situ Formed Alumina Interfacial Layer

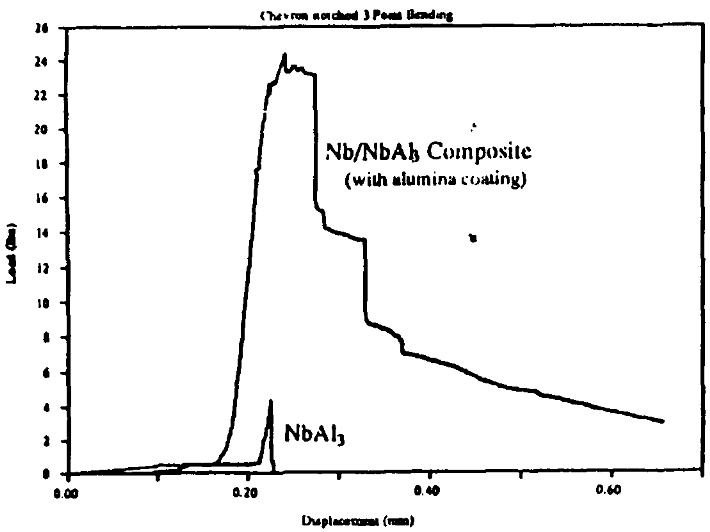
SEM Micrograph.

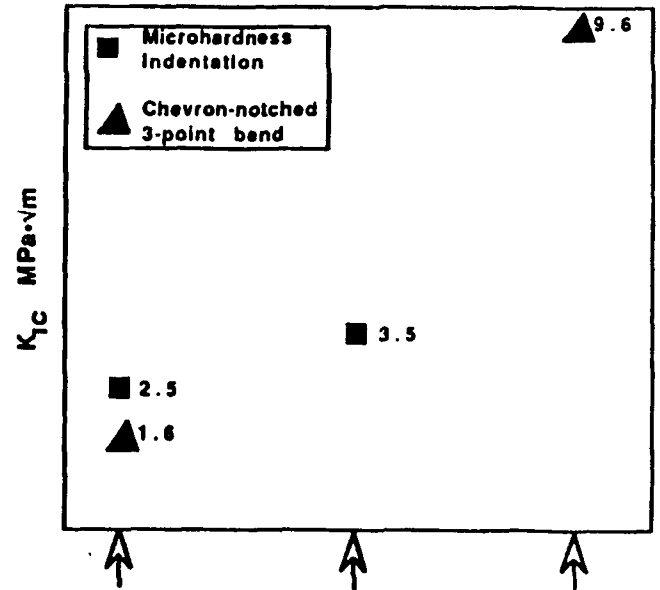


TEM Micrograph



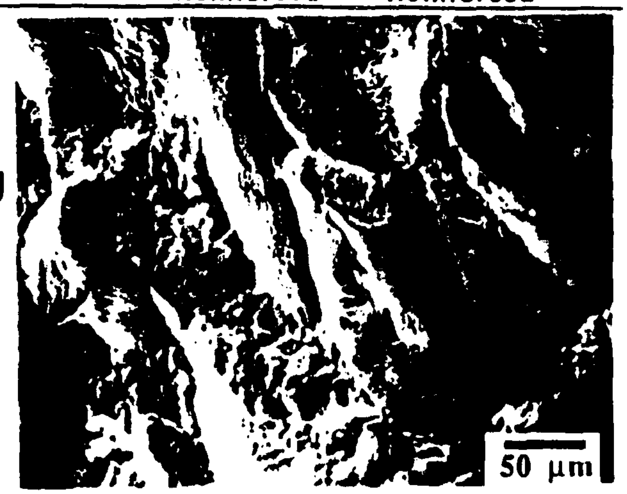
Toughening Effect of Nb Filament Reinforcements With Alumina Diffusion Barrier Produced "In-Situ"





Toughening Due to Interfacial Debonding

Toughening Due to Filament Pull-Out



$NbAl_3$ -- Matrix Development

Highlights

- Additions of Fe, Ni, Ti, V, Cu, Cr and Pd were investigated for possible "ductilizing" effects. In many cases, the segregation during solidification is severe.
- Only marginal improvements in toughness are possible by alloying to form second phases.
- Lamellar eutectics were observed in the Al-Nb-V and Al-Nb-Cr systems.
- Corrections were proposed for the ternary Al-Nb-V isotherm.
- Formation of alumina on niobium filaments using prealloyed $NbAl_3$ powders was successful.
- Alloying to promote the $DO_{22} \rightarrow L1_2$ transformation is not possible for this compound.

NiAl-Matrix Composites

RHC studies

- Effect of processing schedule
- DTA to investigate enthalpy changes during processing

Interface development

- Alumina formation on niobium reinforcements
- Carbide formatlion on Mo and W reinforcements
- Interface formation on selected fibers

Property measurements

- Influence of refractory metal diameter on mechanical properties
- Interface strength compared with uncoated reinforcements
- Composite properties vs. reinforcement schemes

Reaction Schemes for NiAl Matrix Composites

Extension of Nb/NbAl$_3$ Work

$NiAl + Nb/Nb_2O_5 \rightarrow NiAl/Al_2O_3/Nb$

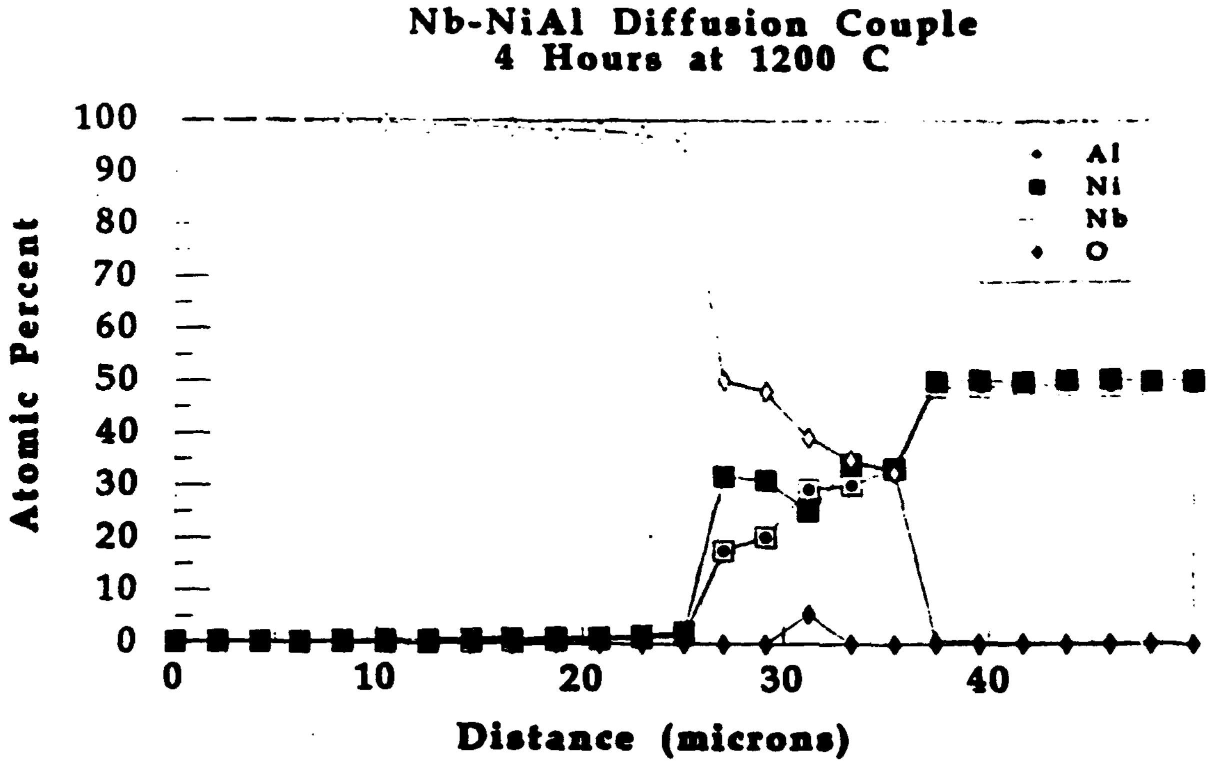
Related Approaches for Molybdenum & Tungsten Reinforcements

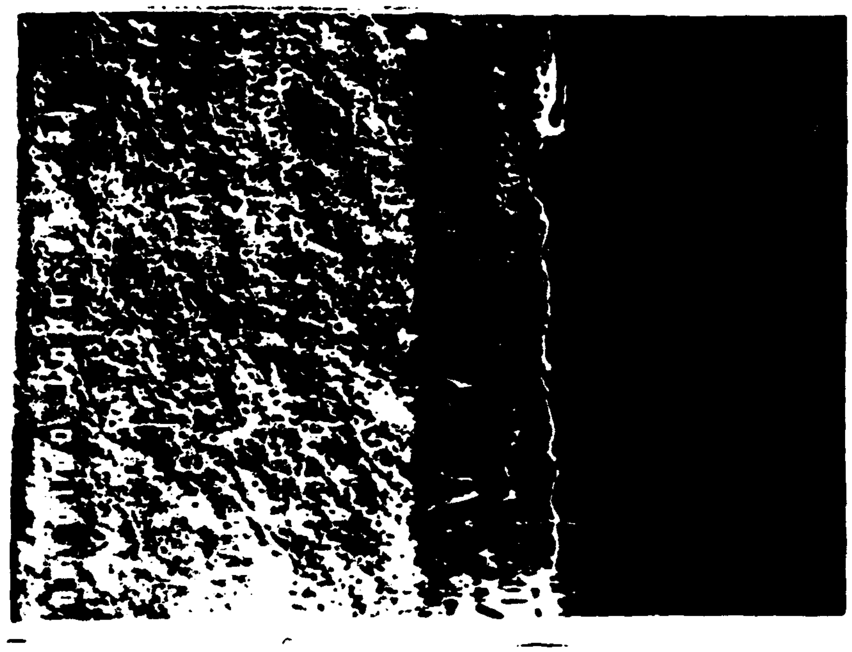
$NiAl(C) + Mo$ or $W \rightarrow NiAl/Mo_2C/Mo$ or $NiAl/W_2C/W$

$NiAl + Mo/Mo_2C$ or $W/W_2C \rightarrow NiAl/Mo_2C/Mo$ or $NiAl/W_2C/W$

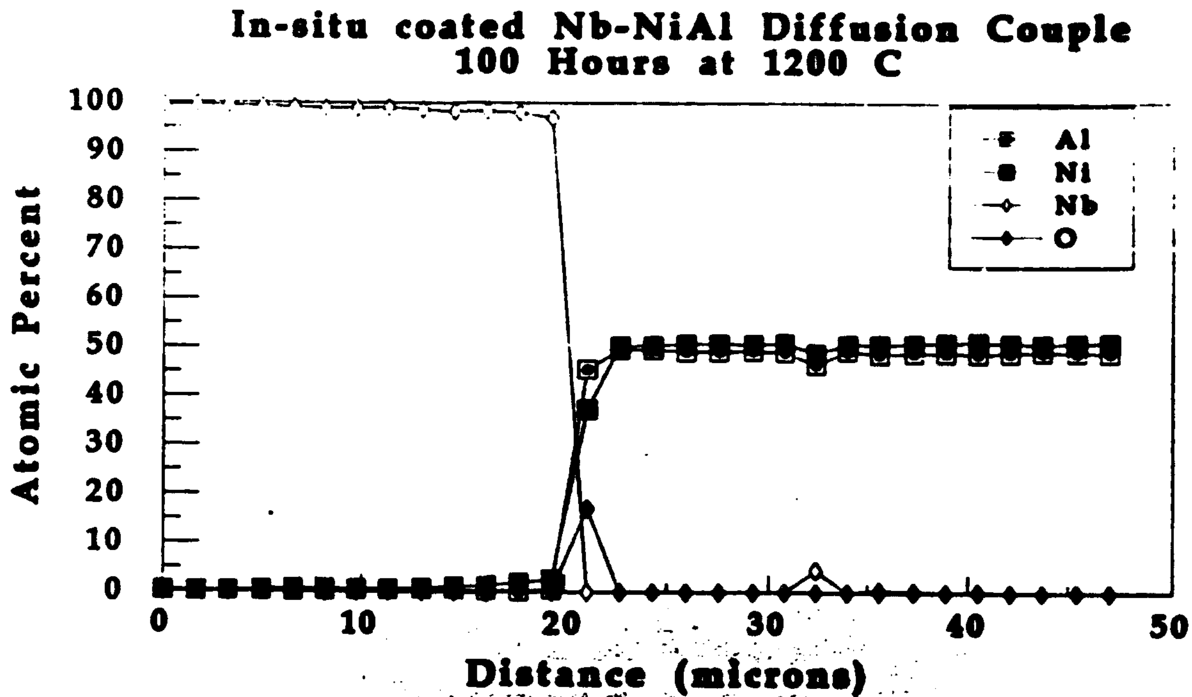
Related Approaches for Sapphire Reinforcements

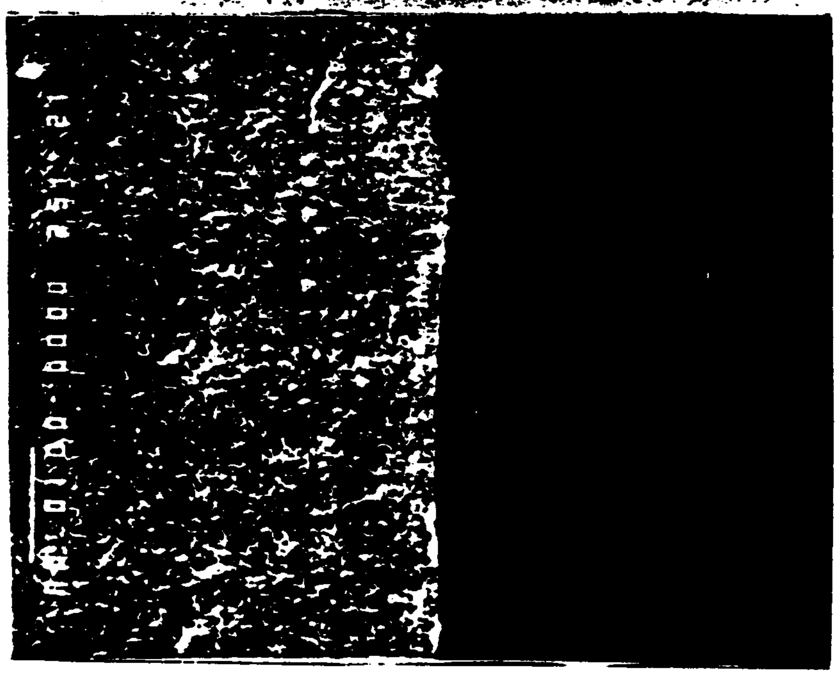
$NiAl(Si)$ + Sapphire $\rightarrow$ NiAl/Mullite/Sapphire



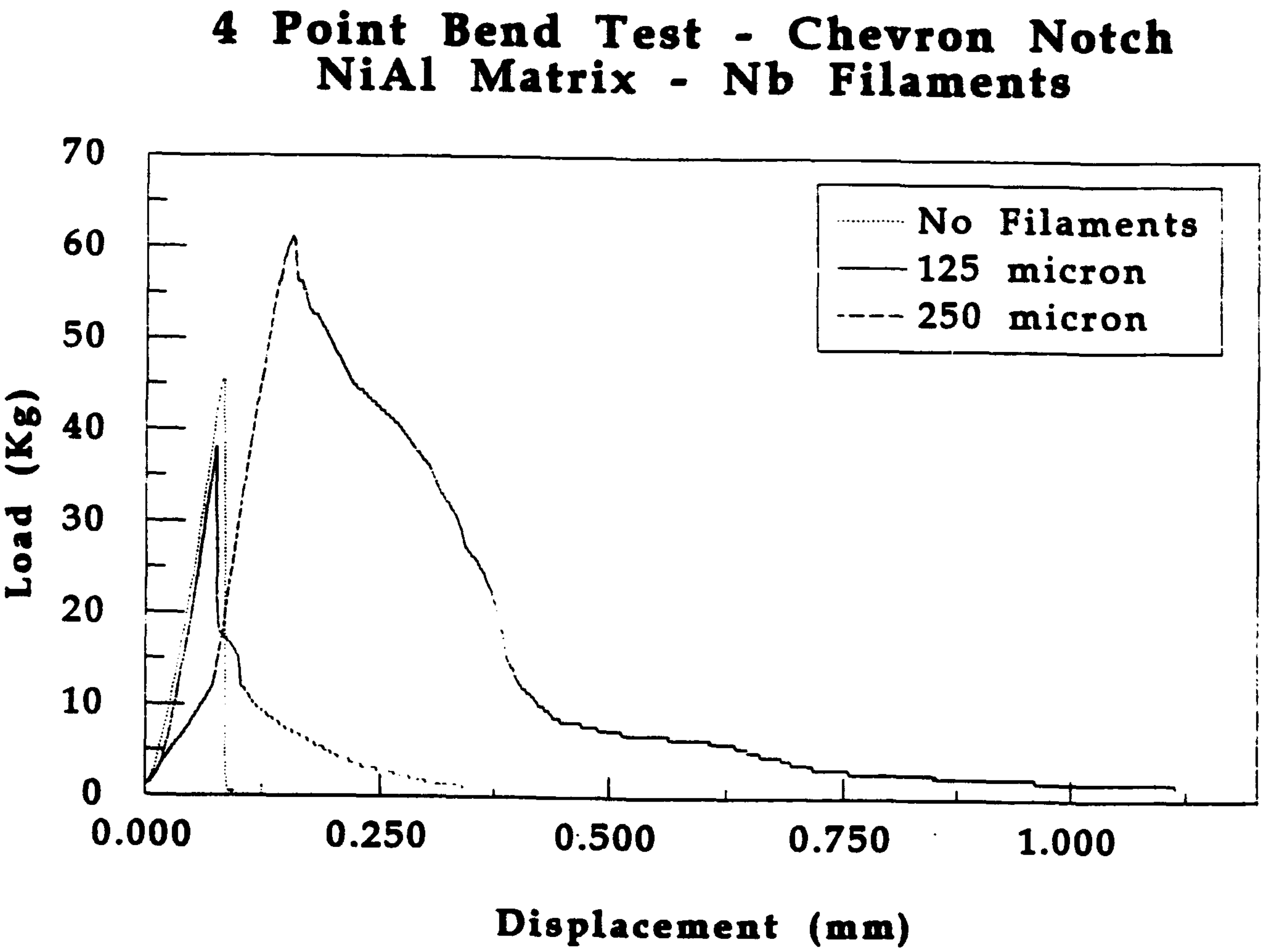


Electron microprobe linescan showing extensive reaction zone between the NiAl matrix and untreated niobium reinforcement.





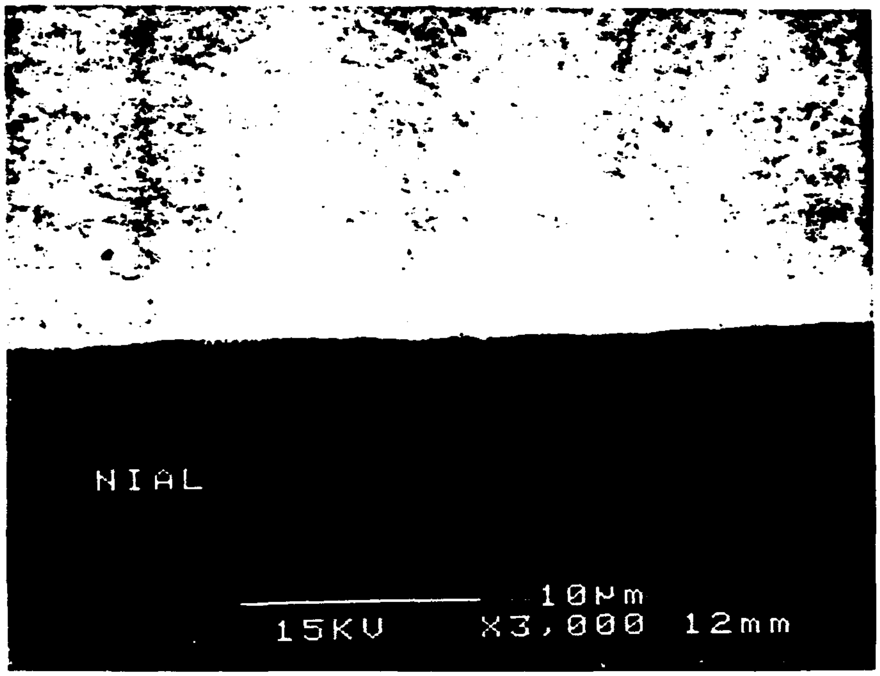
Electron microprobe linescan showing reactively formed alumina interface between NiAl matrix and pretreated niobium reinforcement.

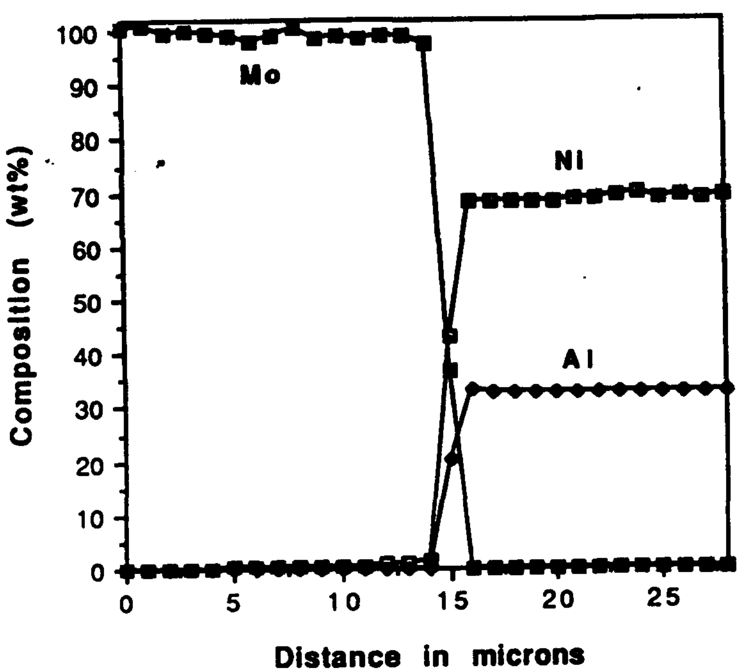


SAMPLE	K_{IC} (MPa√m)	FRACTURE ENERGY (J/m²)
00-000	11.03 ± 1.09	1253.6 ± 289.6
00-125	7.15 ± 1.21	1481.5 ± 183.0
00-250	12.75 ± 1.62	6794.8 ± 2157.9

INTERMETALLIC MATRIX COMPOSITES

NiAl / Mo diffusion couple





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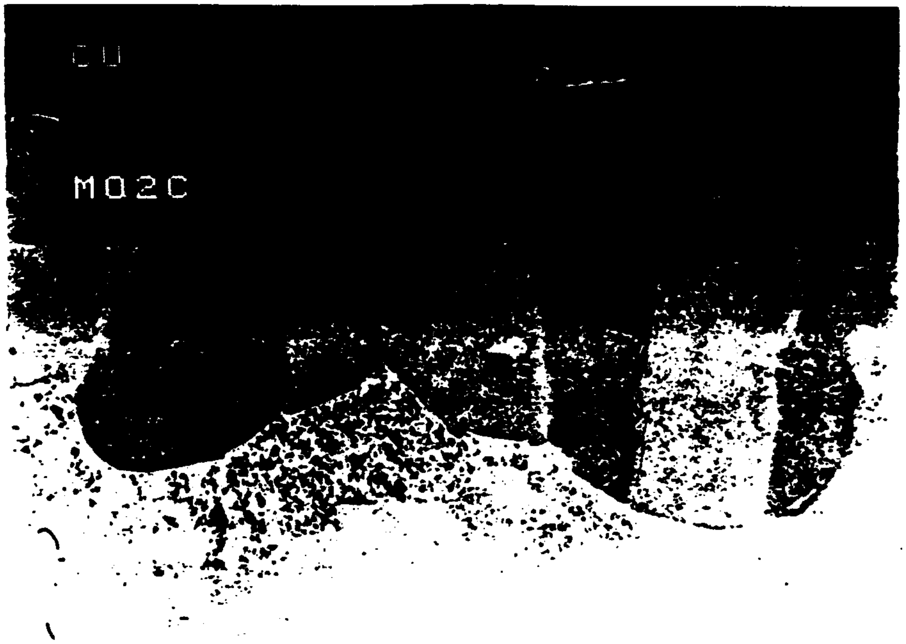
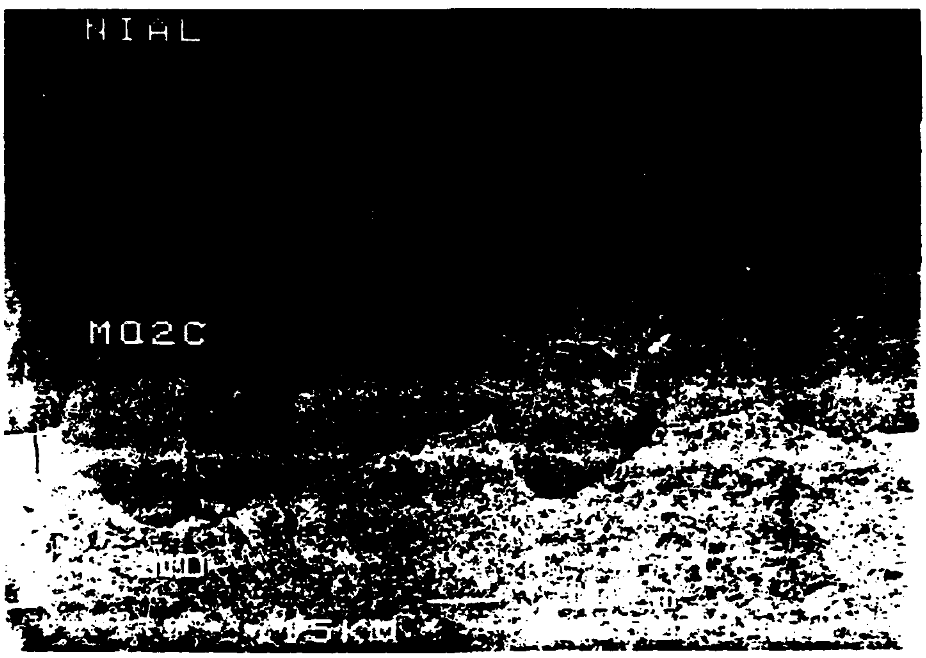
INTERMETALLIC MATRIX COMPOSITES

Precarburized molybdenum



NiAl / Mo_2C / Mo diffusion couple



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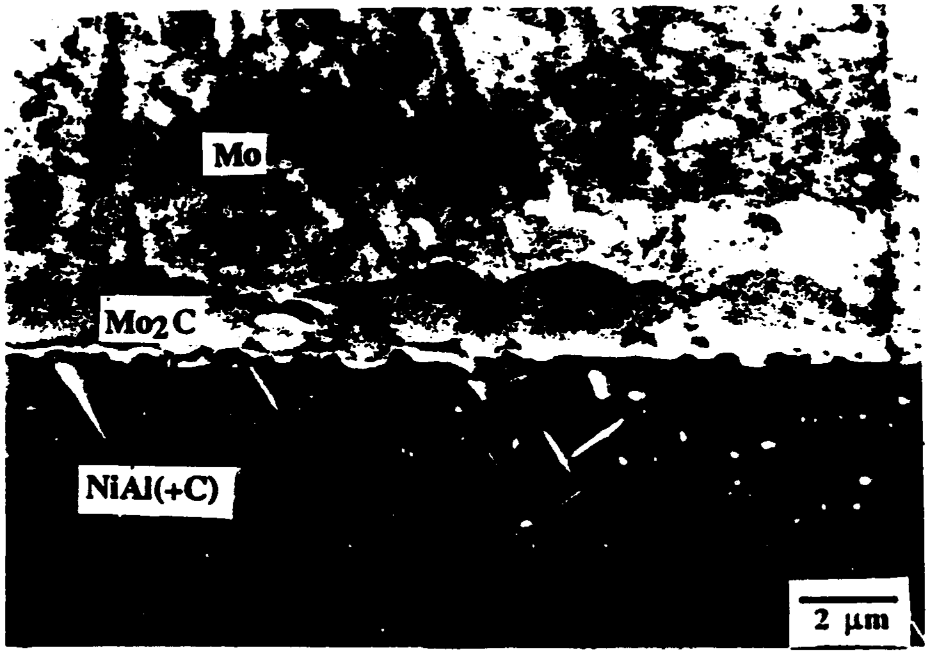
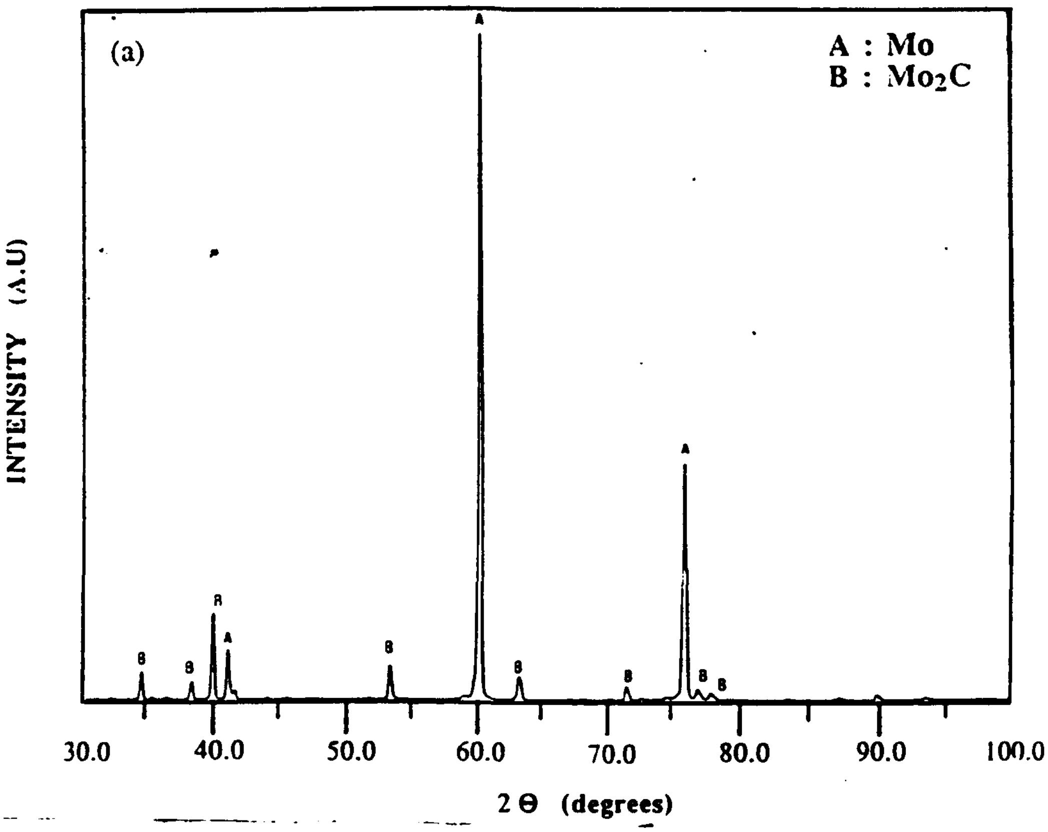
INTERMETALLIC MATRIX COMPOSITES

DARPA

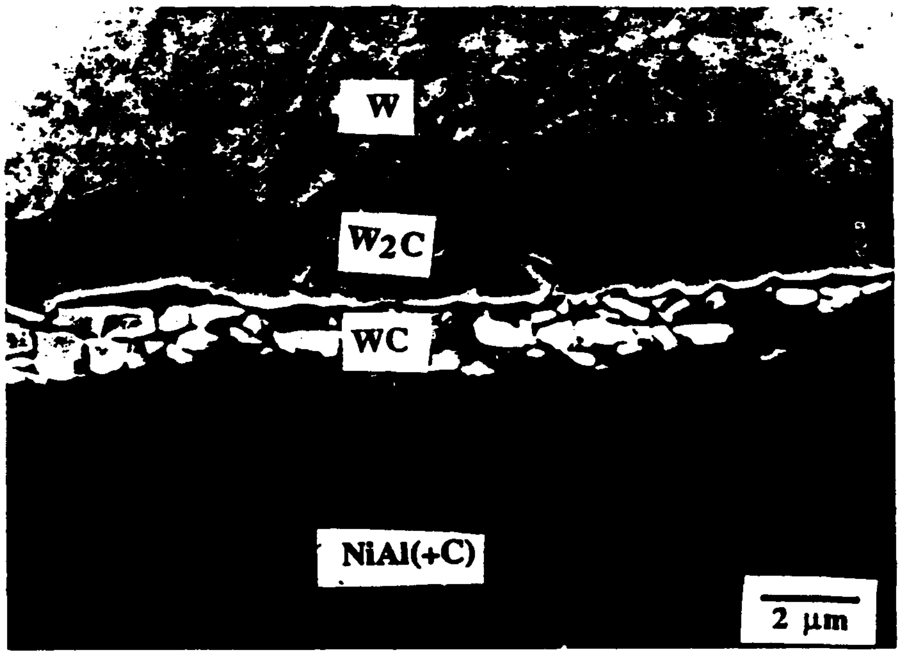
NiAl(+C) / Mo diffusion couple

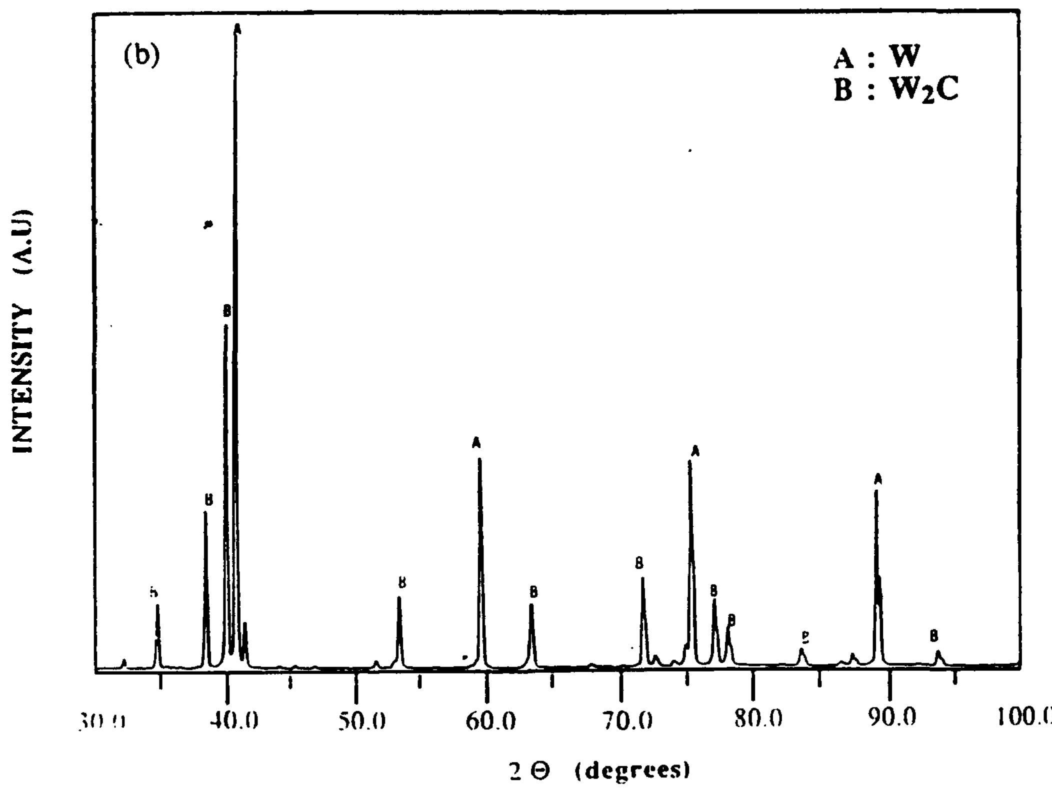




INTERMETALLIC MATRIX COMPOSITES

NiAl(+C) / W diffusion couple





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$MoSi_2$ Studies

Ductile phase toughening studies Chemically stable

- Niobium/$MoSi_2$ laminates
- Coating studies
- Modeling

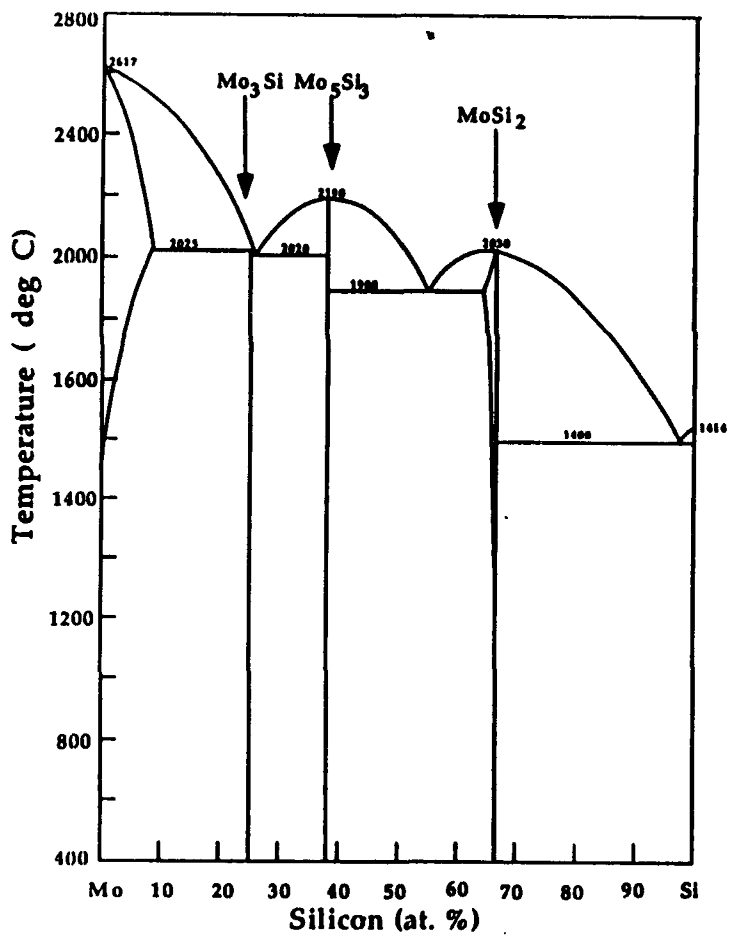
Matrix development

- Tape casting of $MoSi_2$ containing SiC whiskers
- Mechanical alloying -- carbon additions for reducing silica and forming SiC dispersion
- Microstructural evolution of carbon-modified materials

Thermochemistry studies

- Estimation of Mo-Si-C phase equilibria using existing thermochemical data
- Verification by microstructural analysis

Physical Properties of $MoSi_2$



(From Brewer and Lamoreaux, 1980)

Density : 6.14 g/cc

Elastic Modulus : 380 GPa

Poissons Ratio : 0.17

Hardness : ~ 1300 kg/mm^2

Thermal Conductivity : 0.49 W/cm°C

Excellent Oxidation Resistance

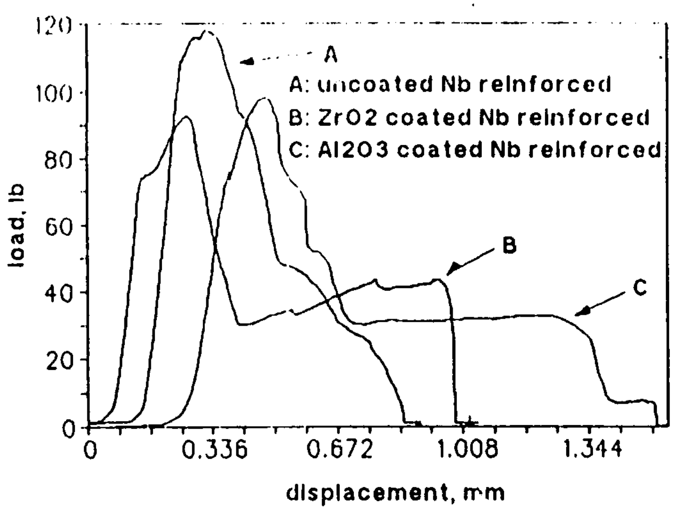
Fracture Toughness : 3 ~5 $MPa\text{-}m^{1/2}$

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

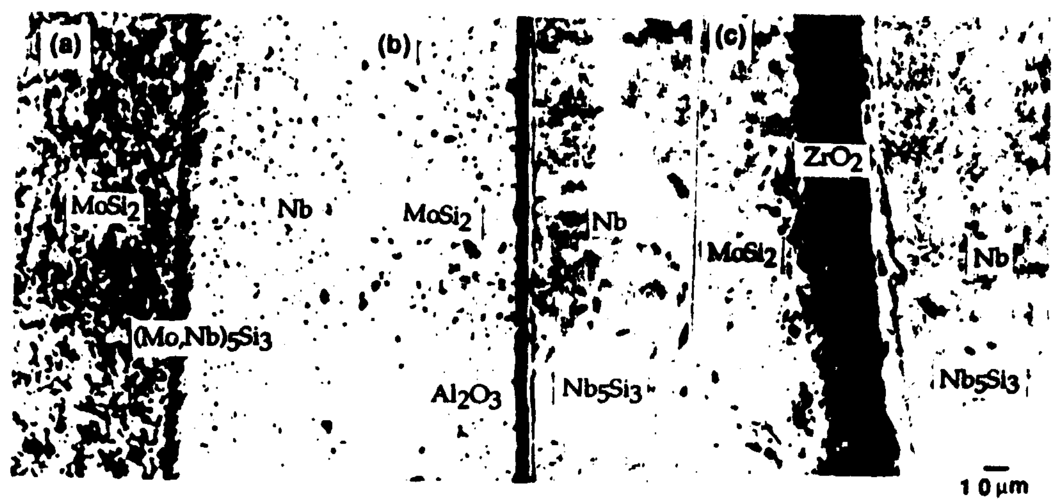
Toughness and Interfacial Fracture Energy of $MoSi_2$ Composites with 20 vol.% of Nb Laminae

Materials	$MoSi_2$	uncoated Nb reinforced	Al_2O_3 coated Nb reinforced	ZrO_2 coated Nb reinforced
Interfacial fracture energy (J/m^2)	-	> 33.7 ± 1.4	16.1 ± 1.3	12.8 ± 1.0
Damage tolerance ($MPa.m^{1/2}$)	3.3 ± 0.3	15.2 ± 1.3	14.0 ± 1.5	12.8 ± 1.5
Work of fracture (J/m^2)	690 ± 30	21,600 ± 3,000	28,700 ± 1,900	28,700 ± 4,600

Typical load-displacement curves of the chevron notched specimens with different interfacial conditions



Interfacial microstructures



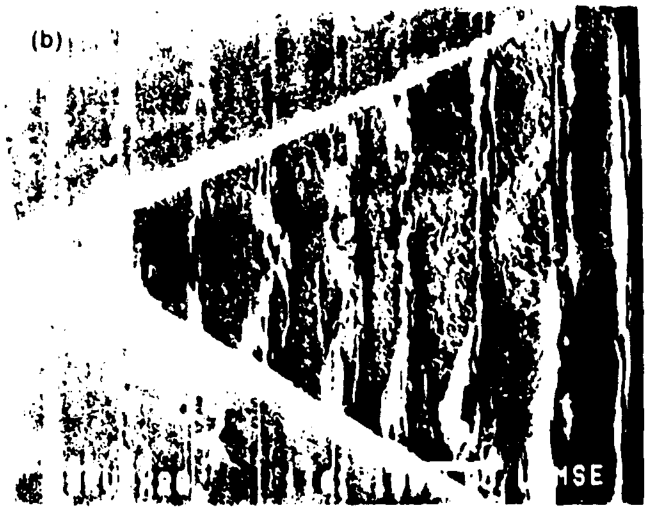
Uncoated Al_2O_3 coated ZrO_2 coated

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Effects of Size of Ductile Phases on Toughness of $MoSi_2$ Composites with 20 vol.% of Nb Laminae

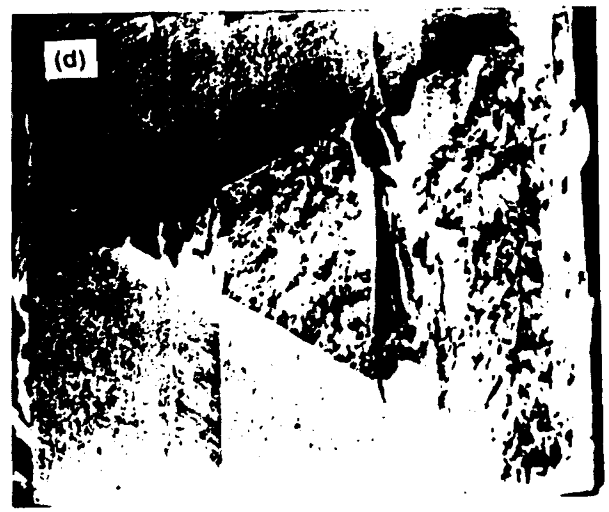
Thickness of Nb laminae (mm)	0.127	0.25	0.5	1.0
Damage tolerance (MPa.m $^{1/2}$)	12.2 ± 0.5	15.2 ± 1.3	15.4 ± 0.6	17.6 ± 0.1
Work of fracture (J/m ^{2})	5,490 ± 200	21,600 ± 3,000	30,900 ± 1,700	35,900 ± 3,500

Fracture Surfaces of the Composite Laminates



Thickness of Nb lamina = 0.127 mm

Thickness of Nb lamina = 0.25 mm



Thickness of Nb lamina = 0.5 mm

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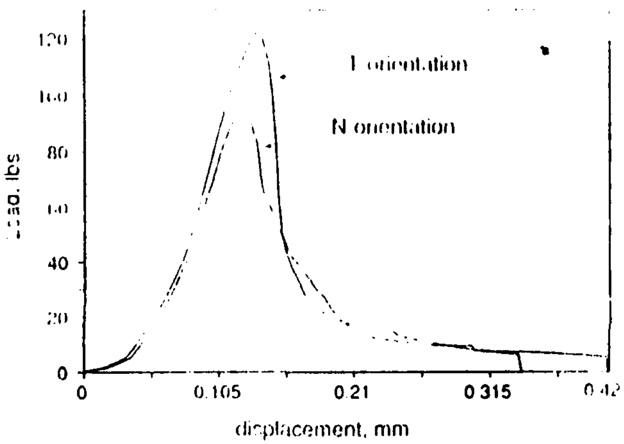
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

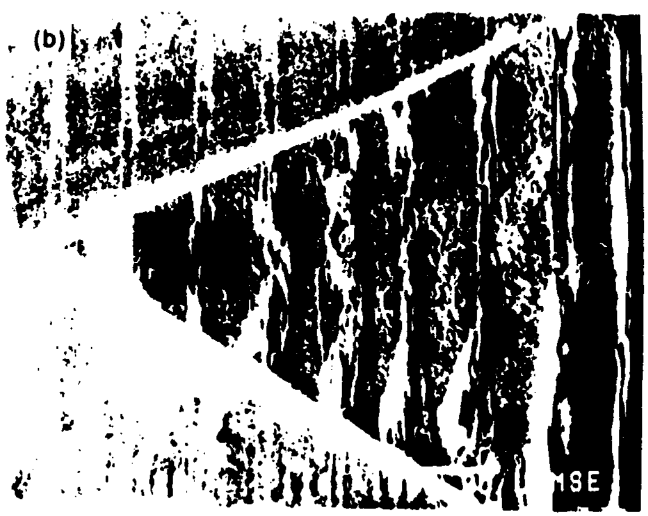
Representative Load-Displacement Curves of Chevron Notched Specimens with Different Orientations



Orientation Dependence of the Toughness of the Composites

Orientation of crack propagation	N	T
Damage tolerance ($MPa.m^{1/2}$)	12.2 ± 0.5	14.9 ± 1.4
Work of fracture (J/m^2)	5,490 ± 200	6,960 ± 350

Fracture Surfaces of the Composite Laminates

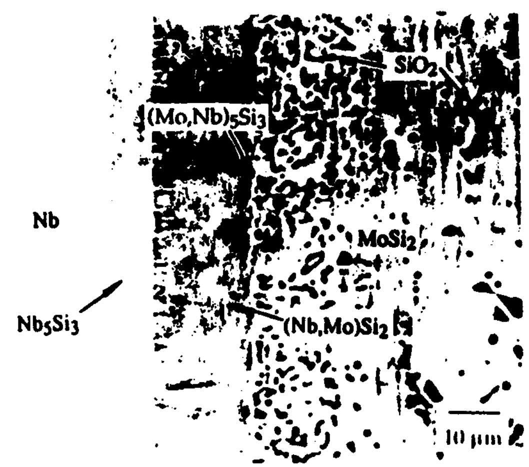


Crack propogates normal to the lamina plane (N-orientation)

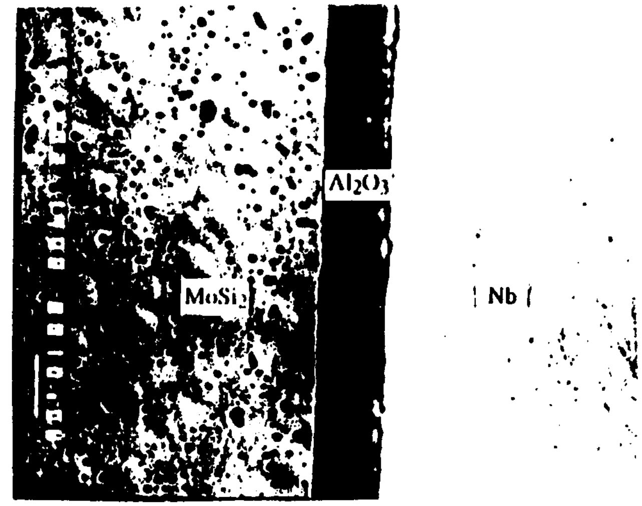
Crack propogates transverse to the lamina plane (T-orientation)

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

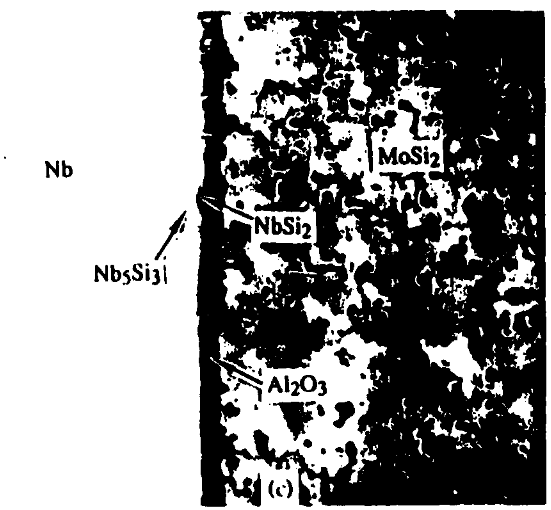
Interfacial Microstructures in $MoSi_2$/Nb Composites



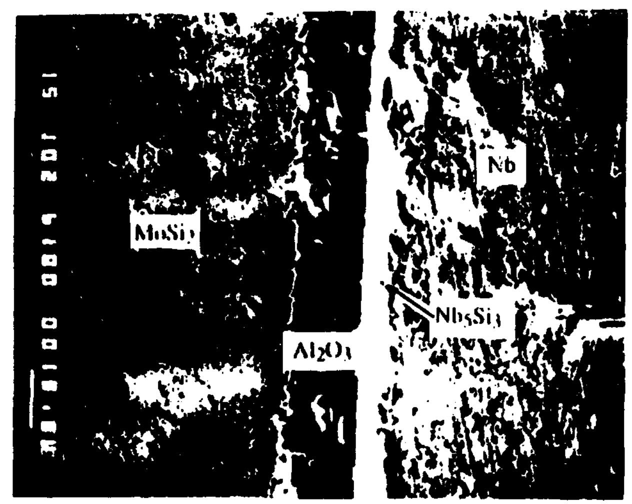
Uncoated



Al_2O_3 coated via sol gel technique



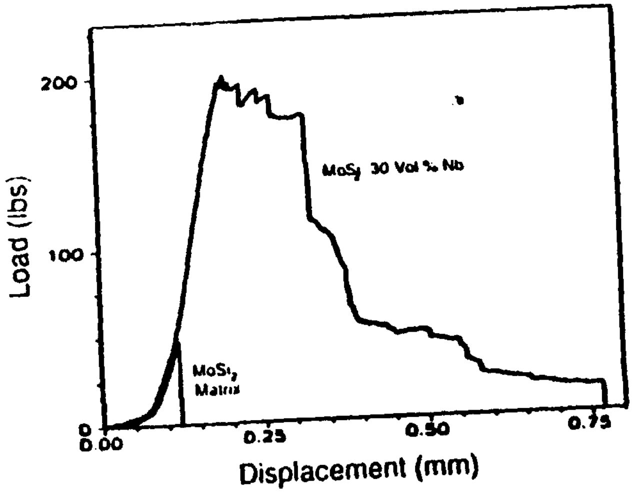
Al_2O_3 coated via PVD

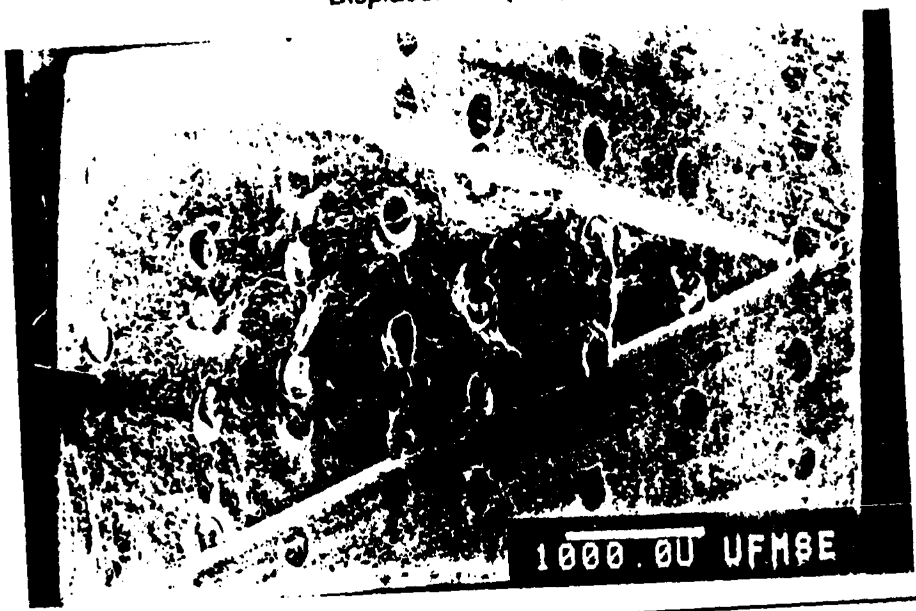


Al_2O_3 coated via aluminum anodizing

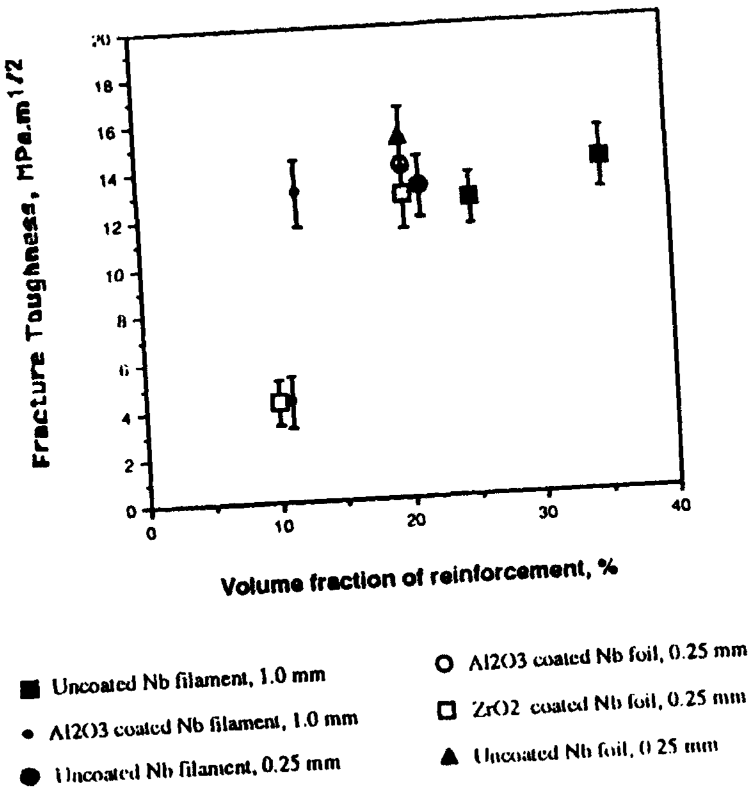
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

load-displacement curves of the Chevron notched samples





Fracture Toughness of $MoSi_2$/Nb Composites



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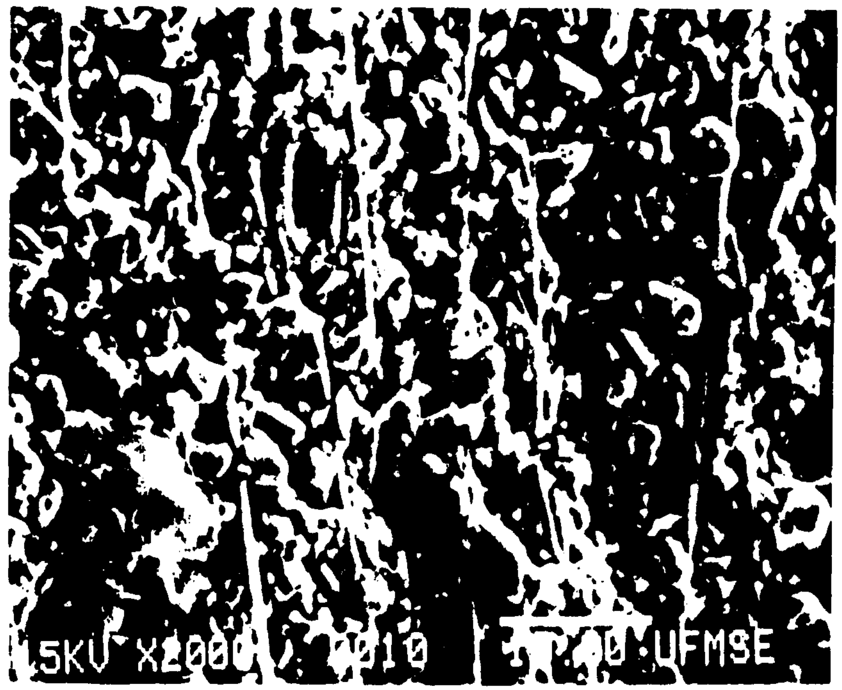
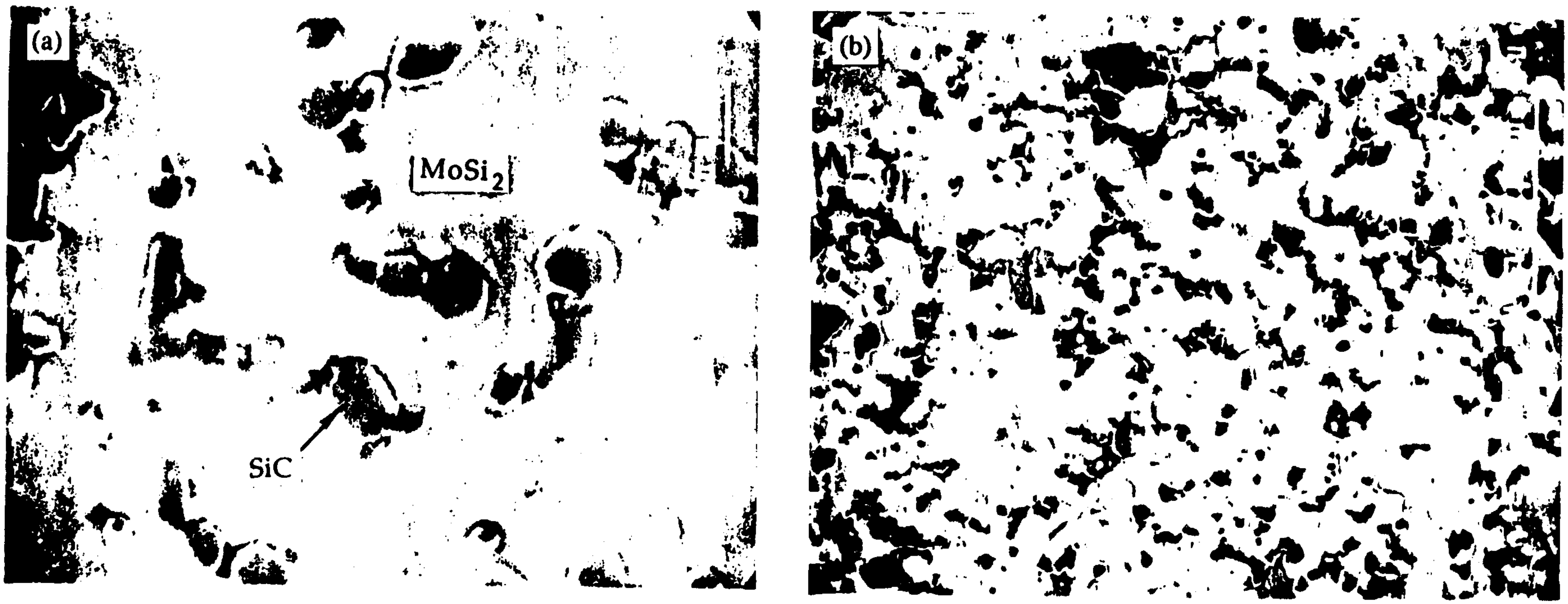
Strengthening of $MoSi_2$ with SiC Whiskers

Incorporation of SiC whiskers was done via tape casting. The incorporation of SiC whiskers is to improve high temperature strength and creep resistance, and at the same time to modify the thermal expansion coefficient of the matrix to enhance ductile phase toughening.



General Image of Green-tape of $MoSi_2$ with 30 vol.% SiC_w

Microstructures of the Hot Pressed $MoSi_2$ Tape With 30 vol.% SiC Whiskers

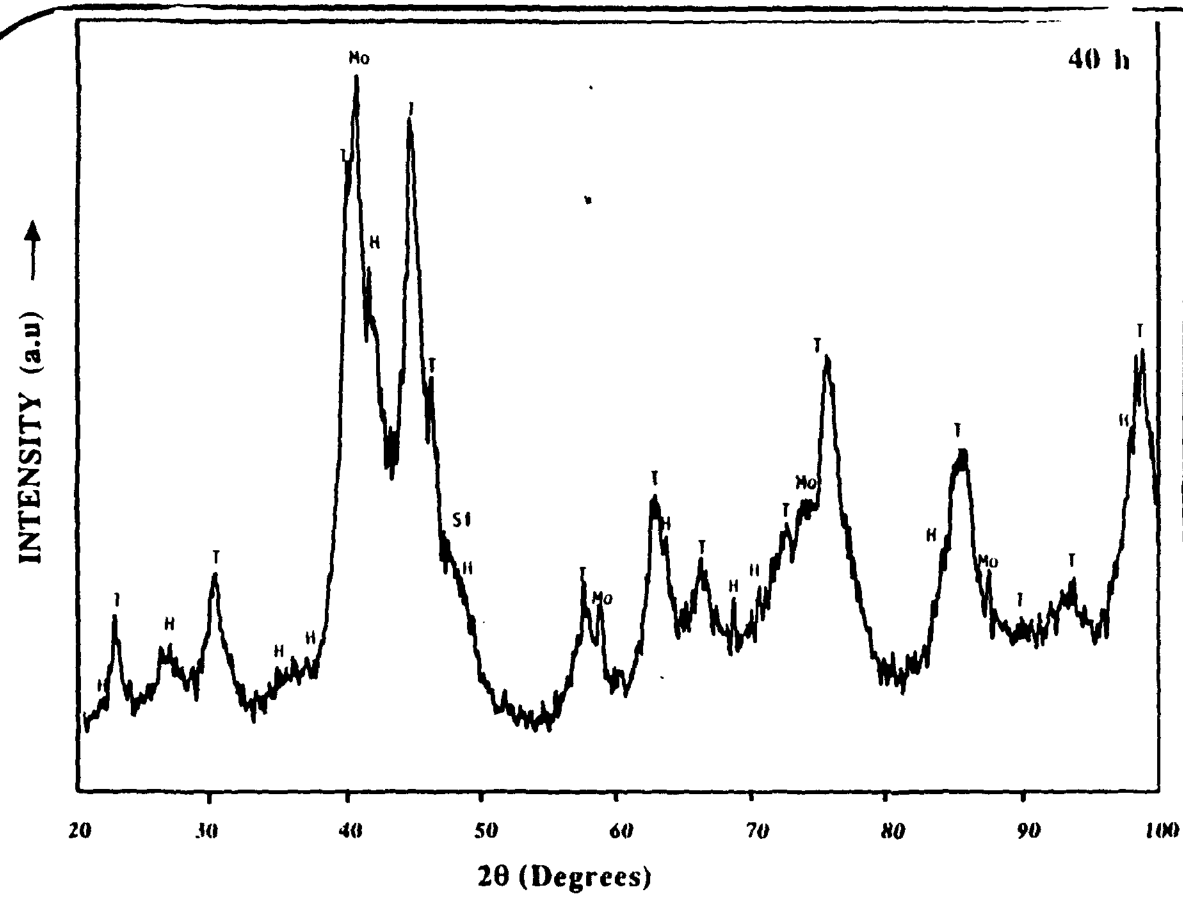


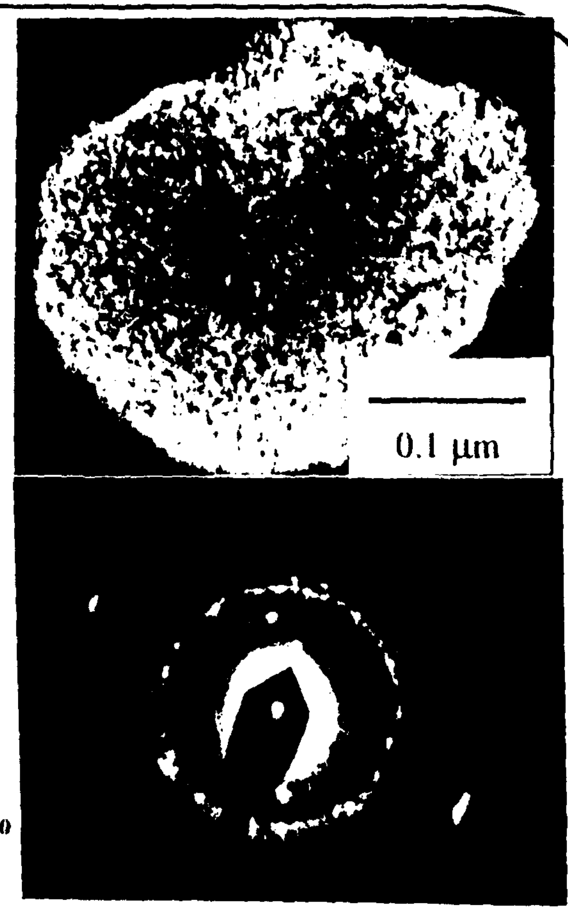
Typical microstructures (SEM) of MoSi -30 vol.% SiC_w composites produced via hot pressing of the tape cast laminae. The cross sections shown are perpendicular to the tape casting direction. (a) Higher magnification view, and (b) overall view of the microstructure.

Why Mechanical Alloying?

- Defects (SiO_2 and/or porosity) in $MoSi_2$ made from commercial powder — $MoSi_2$ can be synthesized at room temperature by mechanical alloying. Carbon can be added to both reduce SiO_2 and form SiC.
- High temperature strength of $MoSi_2$ decreases rapidly at temperatures approaching 1200°C — can use MA to introduce dispersoids into $MoSi_2$.
- Refractory metal toughening is desirable but a problem due to the mismatch in CTE's — can lower CTE of matrix by introducing a uniform dispersion of a lower CTE phase (e.g., SiC) via mechanical alloying.
- High temperatures required to consolidate MoSi2 — can consolidate MA'd powders at relatively low temperatures (e.g., 1200°C)

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS





X-ray diffractogram of a typical powder sample attritted for 40 hours showing the presence of α-MoSi2 (labelled T), β-MoSi2 (labelled H) and molybdenum (labelled Mo). Inset shows a dark field TEM of a powder particle showing a fine distribution of crystallites (4-7 nm) of Mo and α-MoSi2

Reaction Schemes for $MoSi_2$ Studies

Multi-step Reactions

$$SiO_2 \rightarrow SiO + [O]$$

$$C + O \rightarrow CO$$

$$SiO + 2C \rightarrow SiC + CO_2$$

$$SiO + 2C \rightarrow Si\ (\text{silicide}) + CO$$

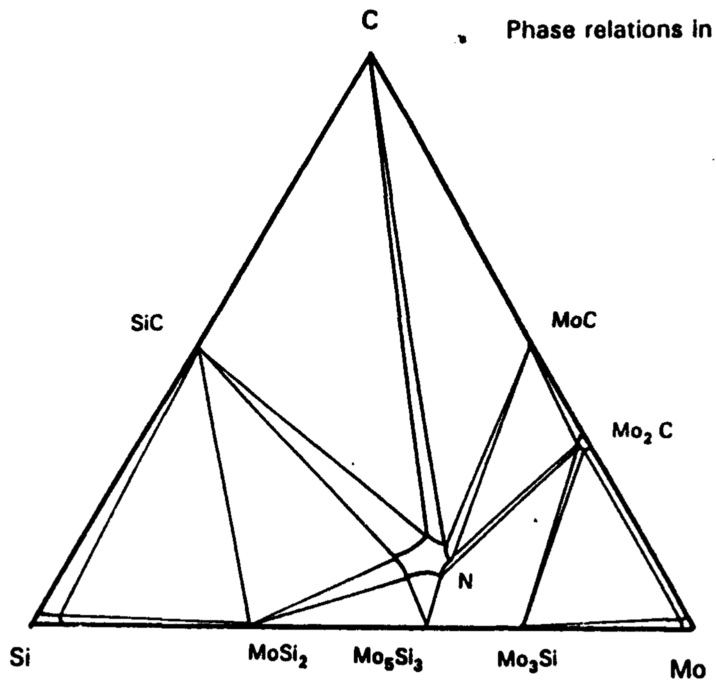
Overall Reaction

$$SiO_2 + 3C \rightarrow Si\ C + 2CO$$

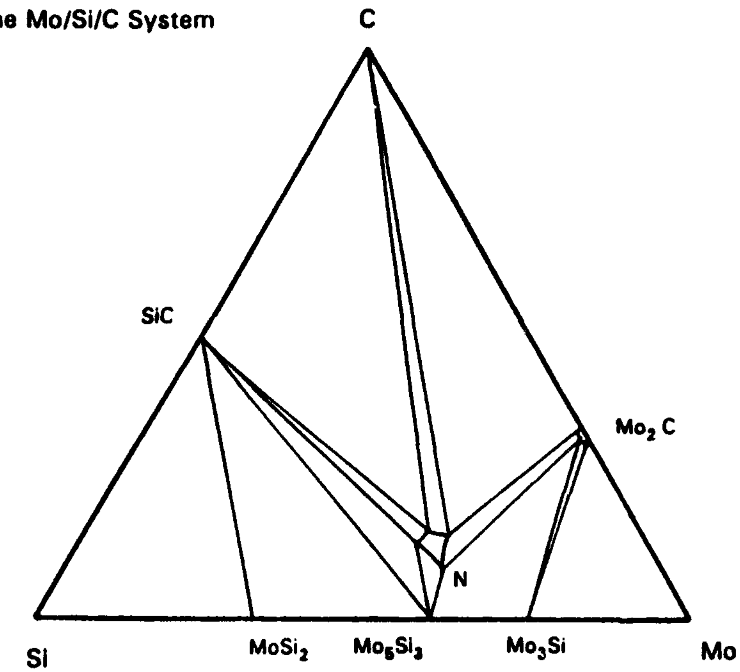
$$SiO_2 + 2C \rightarrow Si\ (\text{silicide}) + 2CO$$

INTERMETALLIC MATRIX COMPOSITES

Phase relations in the Mo/Si/C System



1600°C Isotherm by H.Nowotny et al.
Mh.Chem. 85(1954) 255



1200°C Isotherm by F.J.J.van Loo et al.
High Temp.-High Pres. 14(1982) 25

N = Mo_5Si_3C

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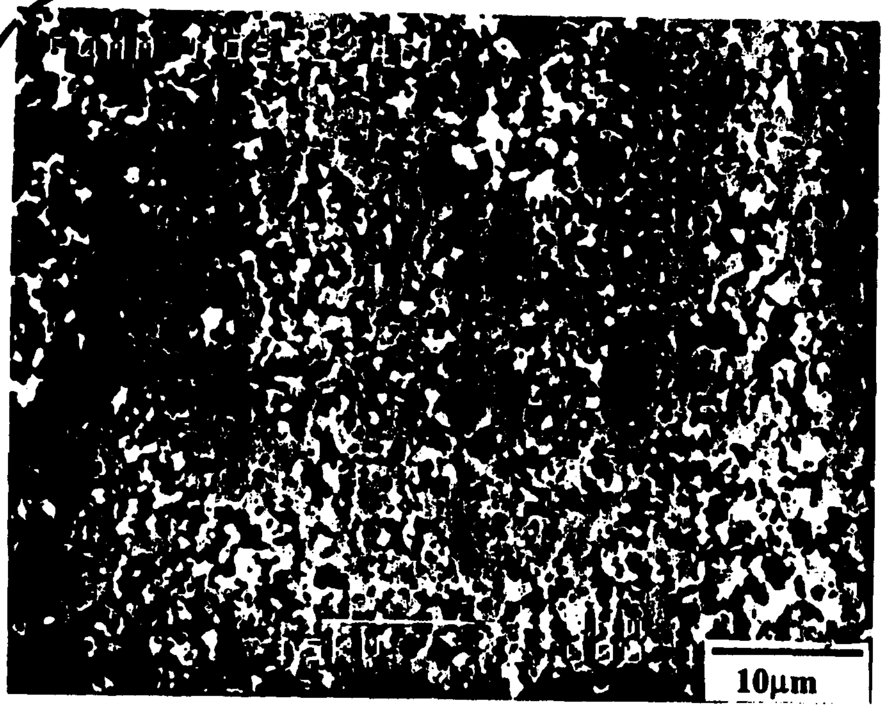
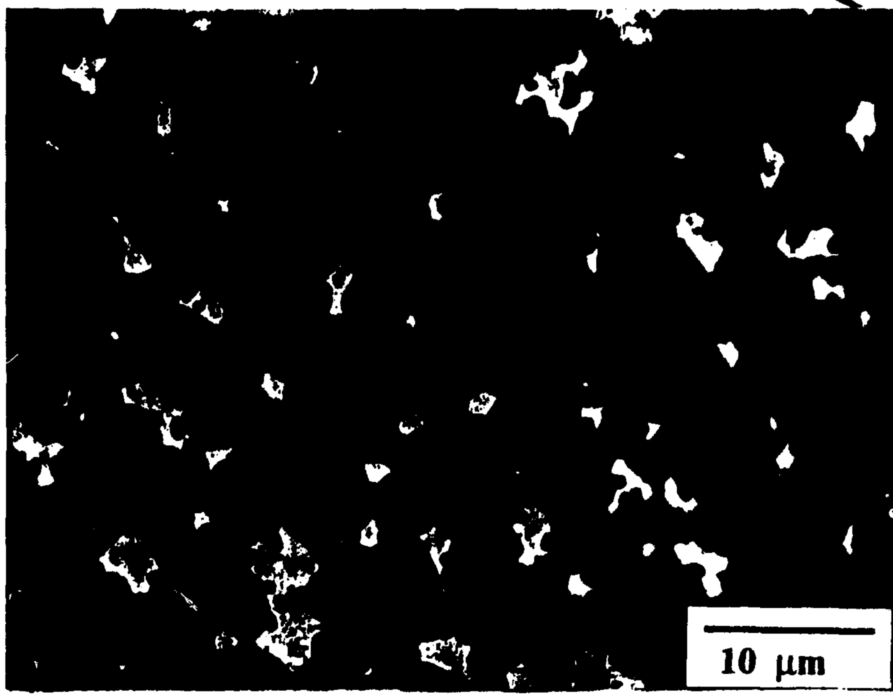
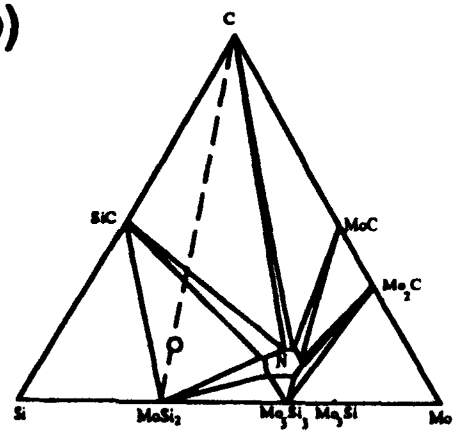


(a)



(b)



Microstructures of carbon-modifed MoSi2 processed using two different approaches, but having the same overall composition as indicated in the isotherm
(a) Commercial MoSi2 + 4 wt.% C, HP @1600°C
(b) Mechanically alloyed powder, Si-28 Mo- 14C (at. %), HP @1600°C. Note the greater degree of homogeneity in the mechanically alloyed microstructure. The white phase is Nowotny phase, grey is MoSi2, and black is SiC.

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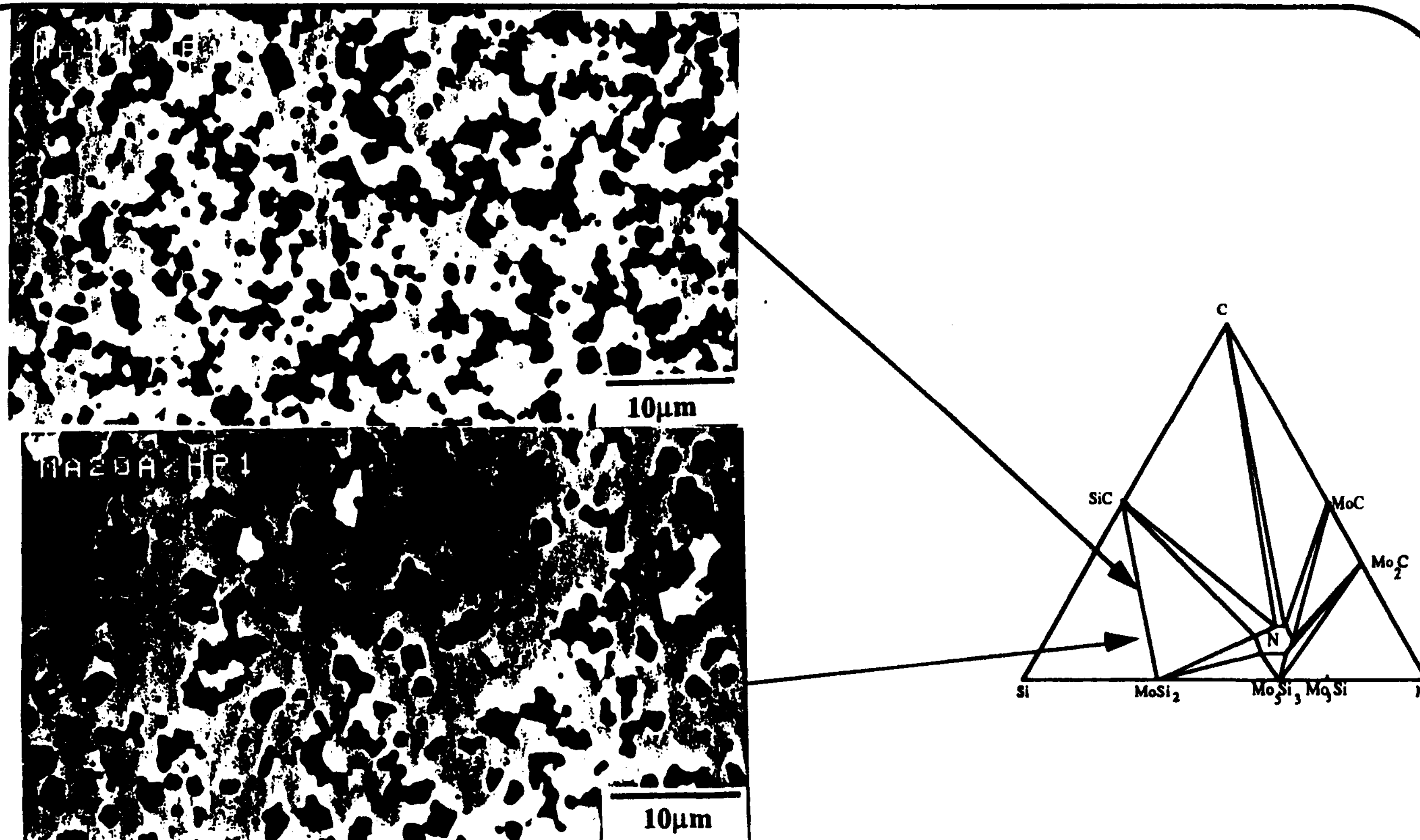
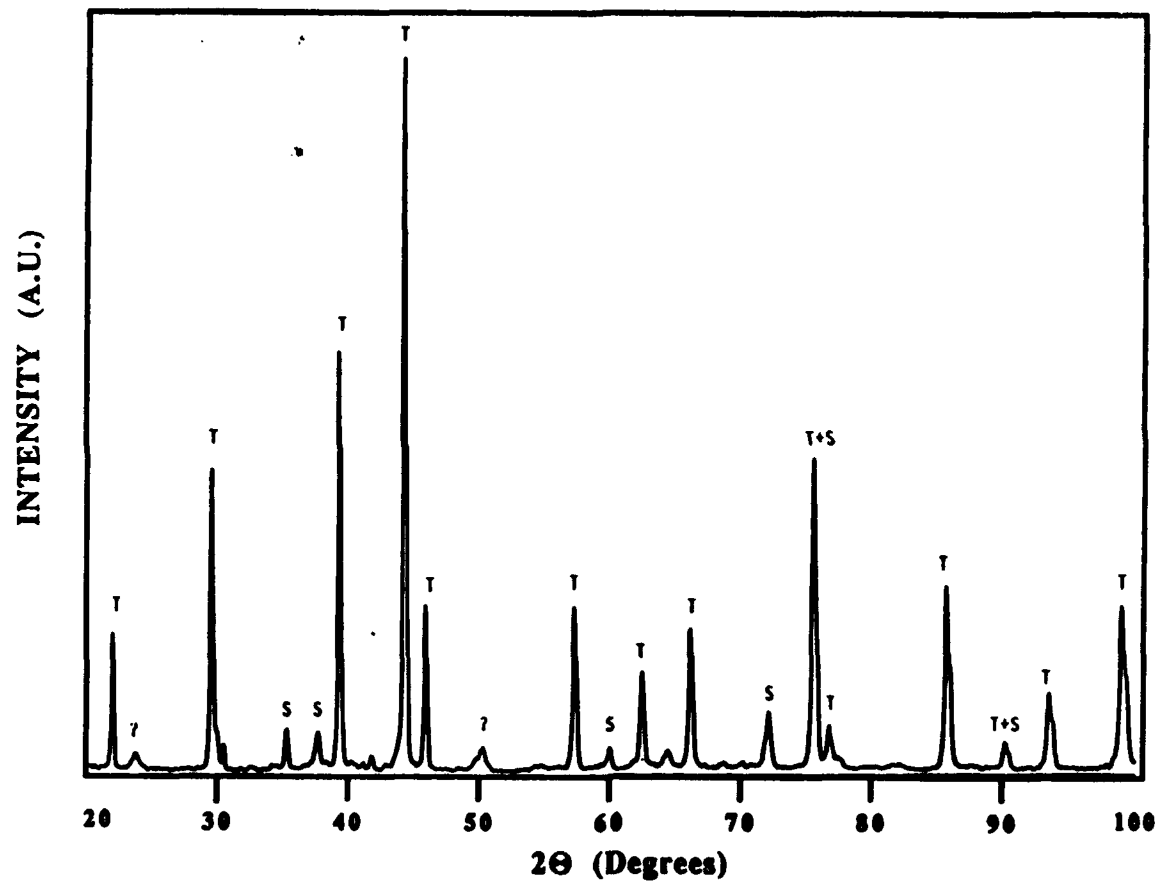
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



Backscattered electron images of the MoSi2/SiC composites processed via the CTDS (Compositionally Tailored Displacive Synthesis) scheme along with the nominal composition of the precursor powders
(a) 40 v/o SiC content (b) 20 v/o SiC content

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



X-ray diffractogram of an in-situ formed MoSi2-20 v/0 SiC composite showing the peaks corresponding to tetragonal MoSi2 (labelled as T) and silicon carbide (labelled as S). Both the α– and β forms are present.

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Bright Field TEM of β-SiC particle formed in-situ in a typical ternary (C-modified) MA MoSi2 sample.

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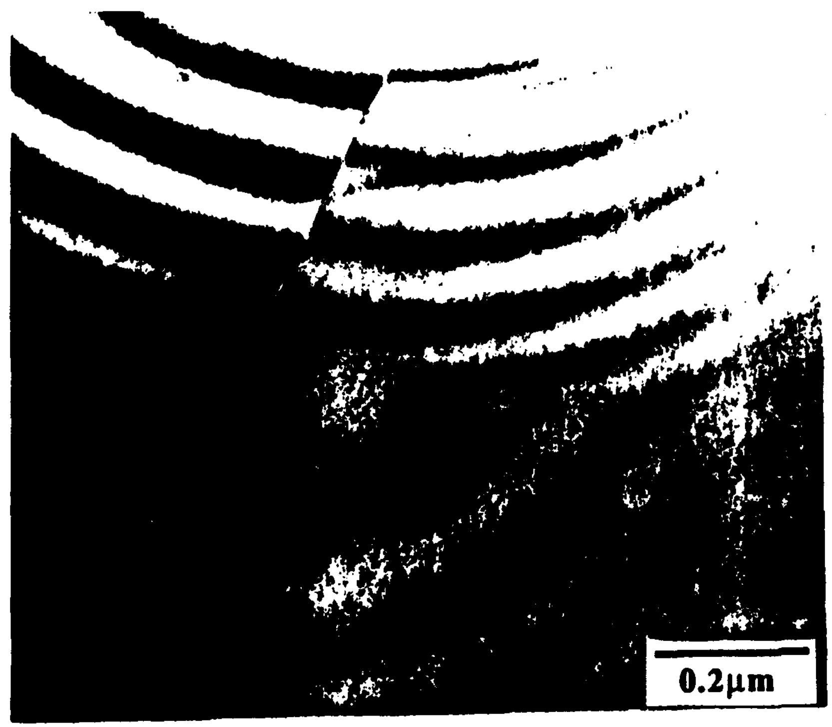
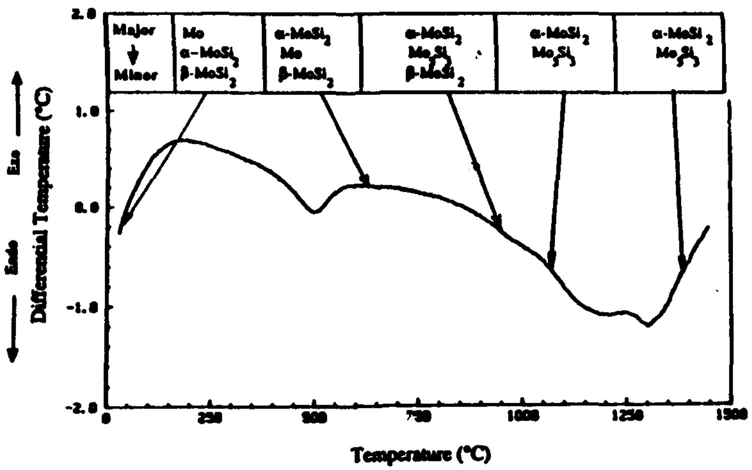
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



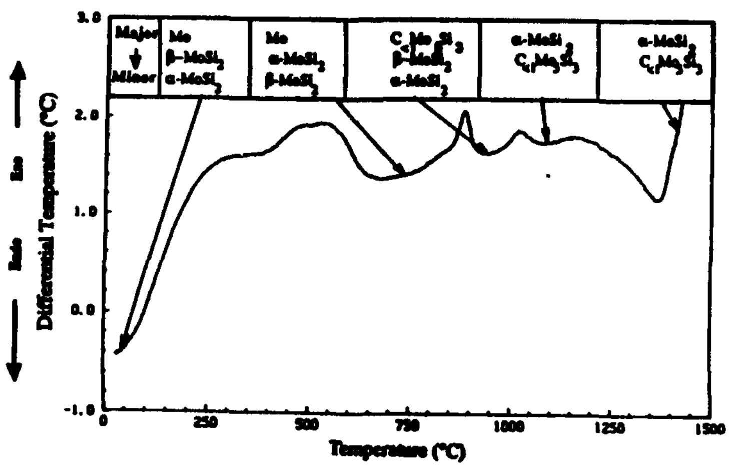
Bright Field Transmission Electron Micrograph of a typical ternary (C-modified) MA $MoSi_2$ showing the clean silica-free grain boundaries

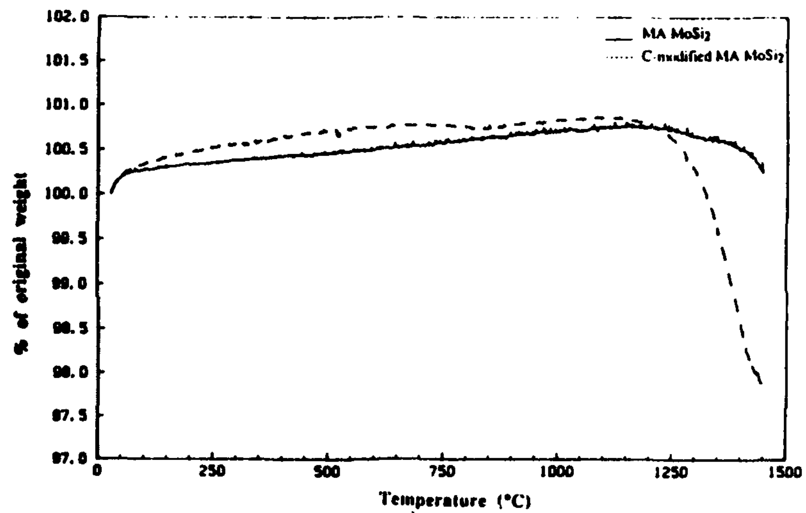
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

(a)



(b)





(c)

(a) DTA of binary MA MoSi2 powder indicating the phase formation sequence
(b) DTA of a typical ternary MA MoSi2. Heating rate 10°C/min under argon
(c) TGA of binary and ternary MA MoSi2 powders, 10°C/min under argon

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INTERMETALLIC MATRIX COMPOSITES

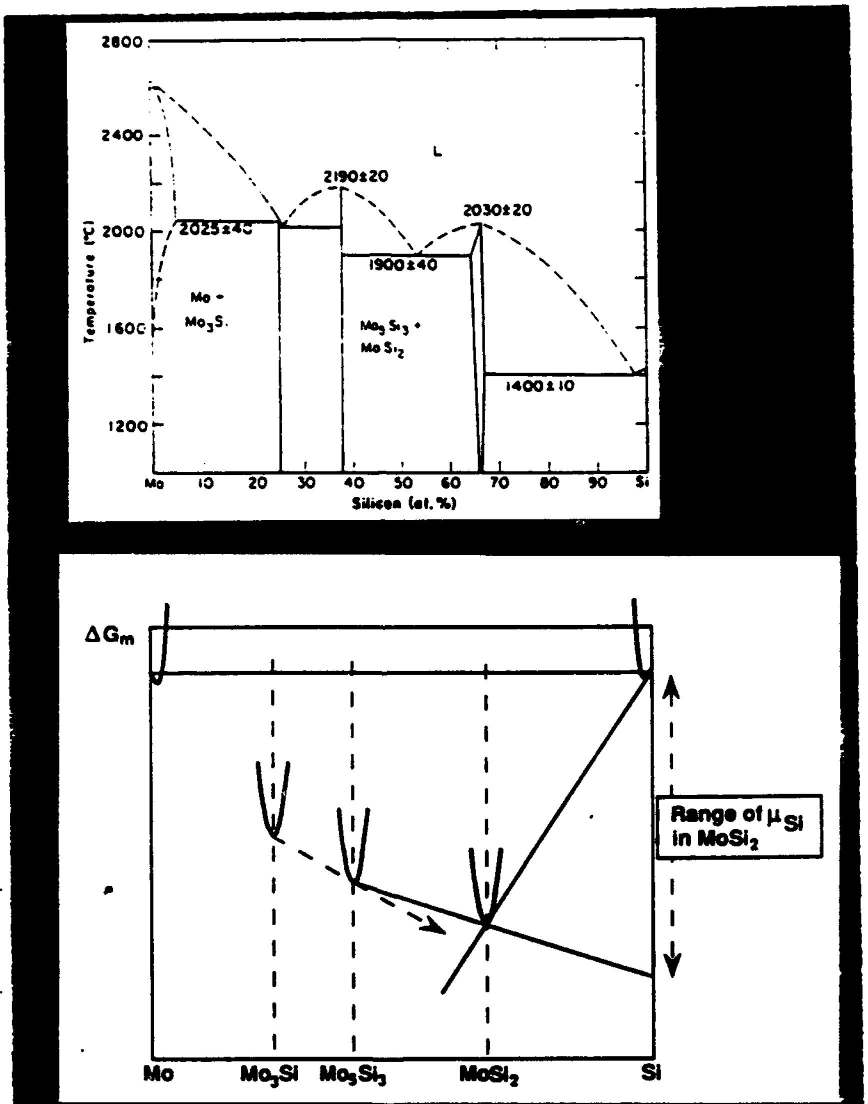


Figure 1 Mo-Si phase diagram (Brewer 1982). Schematic Free energy vs. Composition curves for this system, illustrating the range of silicon activities in $MoSi_2$.

INTERMETALLIC MATRIX COMPOSITES

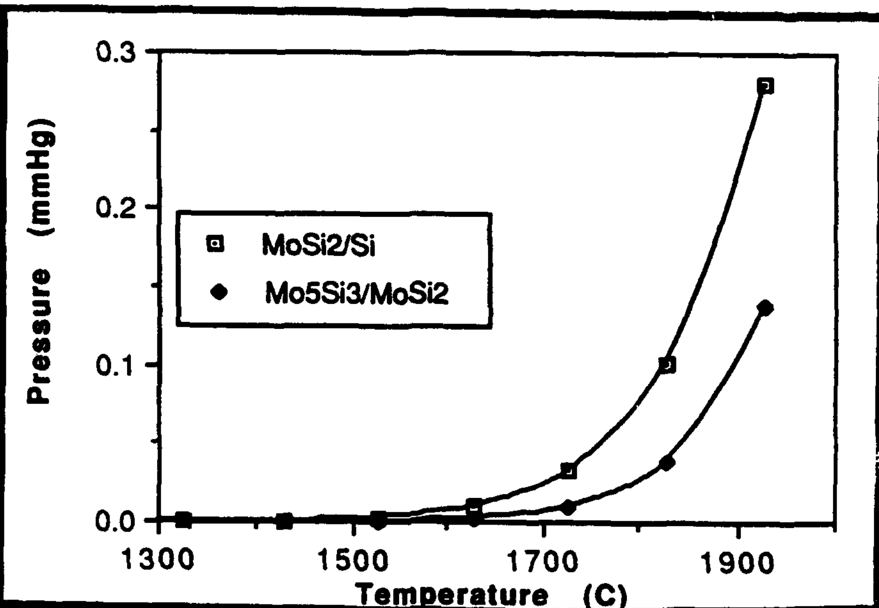


Figure 2 Equilibrium silicon vapor pressure over $MoSi_2$.

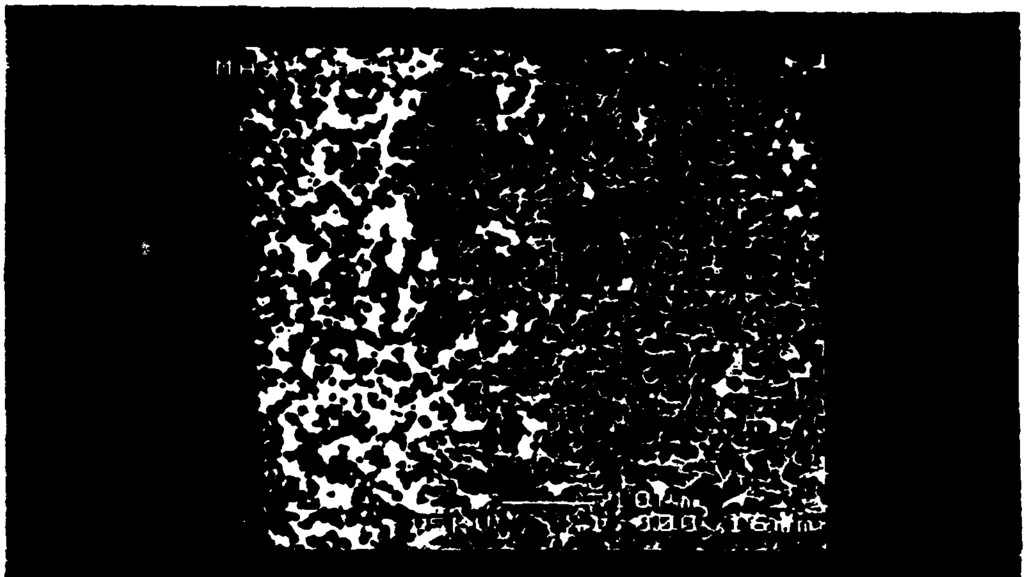


Figure 6 Mechanical alloyed Mo-Si-C vacuum hot pressed at > 1600C. The left side of the picture is close to the sample surface. The phases present indicate this area is poorer in silicon.
(Dark phase: SiC, Gray phase: $MoSi_2$, Light phase: Mo_5Si_3C)

Highlights of $MoSi_2$ Studies

- Under optimized conditions, refractory metal toughening (Nb) leads to damage tolerances approaching 17 $MPa.m^{1/2}$.
- Reliable coating schemes (sol-gel and PVD) have been developed.
- SiC whisker reinforced $MoSi_2$ composites have been produced via tape casting and are being evaluated from the standpoint of high temperature properties.
- Carbon additions to $MoSi_2$ have been used to eliminate silica and to form SiC during consolidation. Both mechanically alloyed and commercial powders have been investigated. For the mechanically alloyed powders, it is possible to produce $MoSi_2$/SiC alloys with much less of the higher Mo phases (e.g., Mo_5Si_3 & Mo_5Si_3C).
- Important processing parameters have been identified and controlled during these studies.
- The phase equilibria in the Mo-Si-C system have been evaluated and the 1600°C isotherm proposed by Nowotny appears to be correct at lower temperatures as well.

Ta-Ti-Al Composites

Hybrid Composites
- Compatibility studies
- Protection of ductile phases (niobium) using in-situ coating
- Processing schemes for fiber alignment
- Property studies

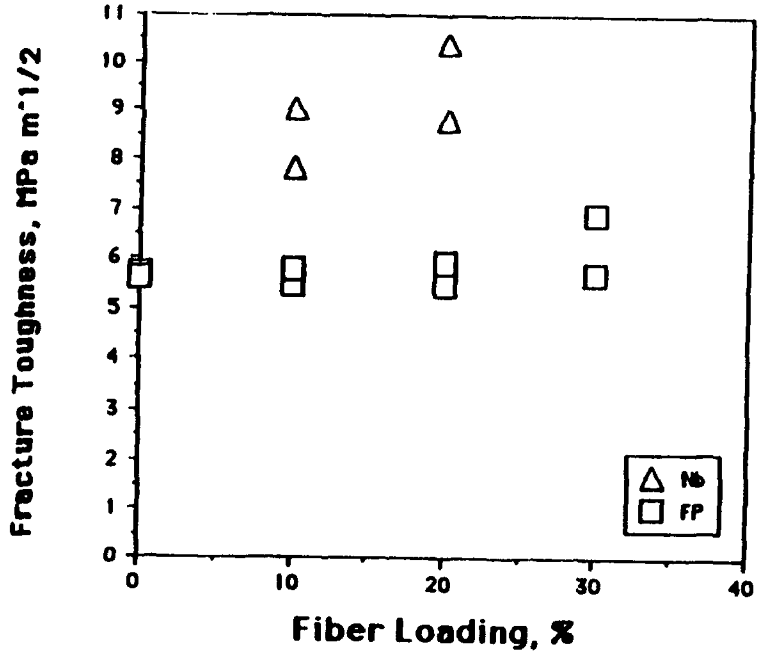
Matrix Development
- Phase equilibria studies
- Phase transformations and matrix optimization
- Microstructure/property relationships

Ta-Ti-Al Hybrid Composites

Highlights

- Alumina was stable with TaTiAl2 alloy
- Short fibers were aligned via cold extrusion
- Composites with in-situ alumina coated Nb fibers exhibit high toughness at room temperature
- FP alumina fiber reinforced composites exhibit higher elastic modulus and flexural strength at 1000 and 1200 C

R.T. Fracture Toughness Values of TaTiAl2 Composites



Matrix/Reinforcement Thermochemical Compatibility

Reinforcement	Interaction	Comments
Al_2O_3	No Reaction	A
Y_2O_3	No Reaction	A
ZrO_2	Moderate	B
ZrN	Extensive	C
ZrC	Extensive	C
SiC	Extensive	C
TiB_2	Extensive	C
Nb	Extensive	D
Nb (alumina coated)	No Reaction	A

Note:
A - *Limited Diffusion Layer*
B - Complex Oxides
C - Reaction Phases
D - Intermetallics

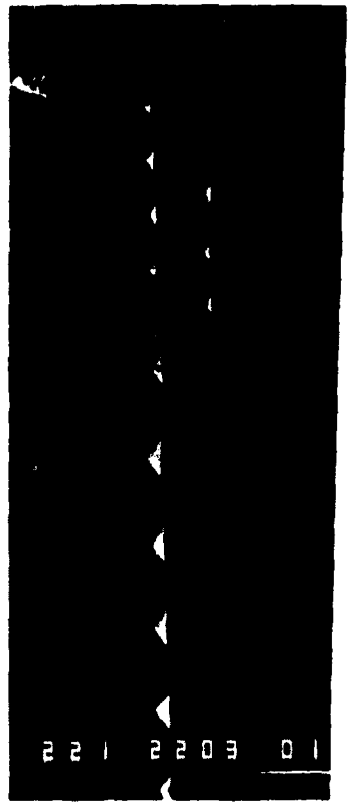
Processing conditions: hot pressed for 30 min under vacuum and annealed for 50 h in Ar atmosphere

Ductile Phase Toughening

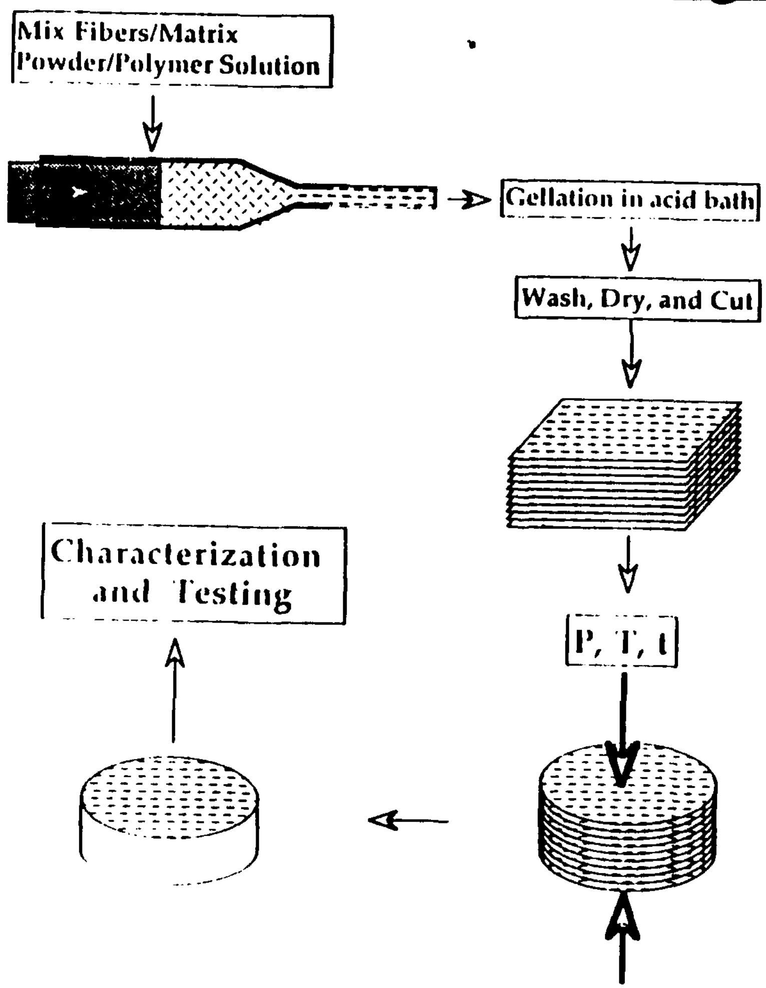
UNCOATED NB FILAMENT

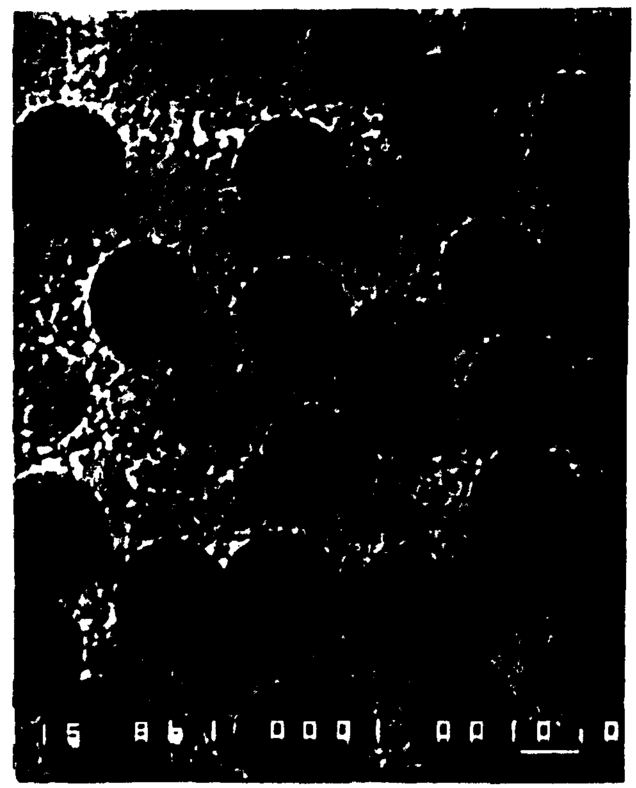
COATED NB FILAMENT

Coated Nb Filament
Microhardness Profiles

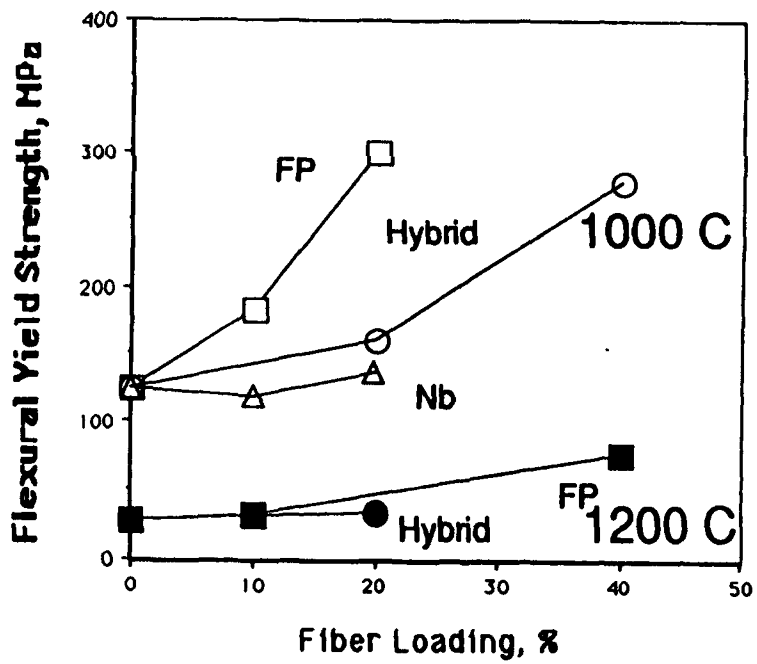


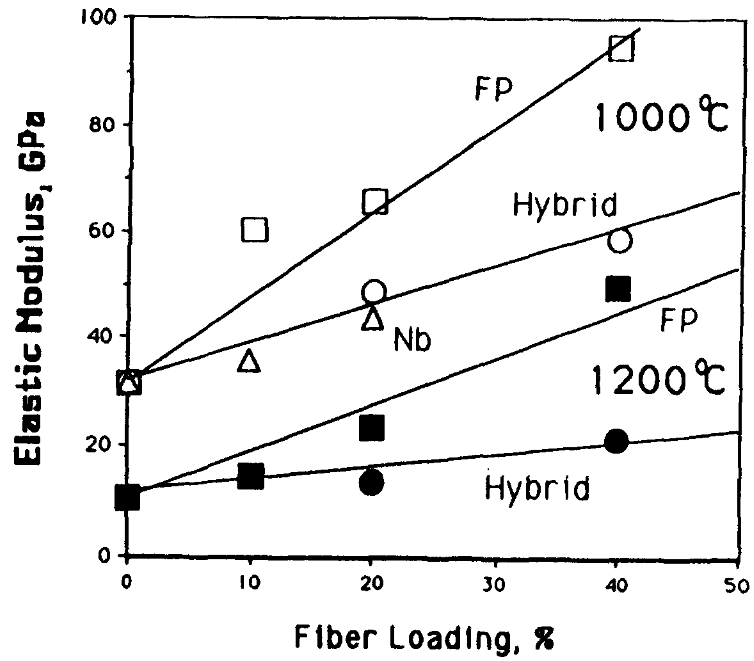
Short Fiber Alignment Process





Flexural Yield Strengths and Elastic Moduli of Composites at High Temperatures





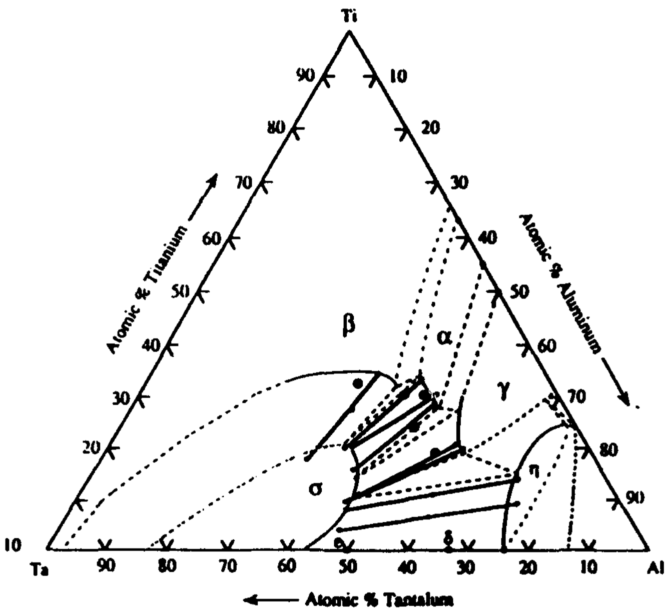
Matrix Development in the Ta-Ti-Al System

Highlights

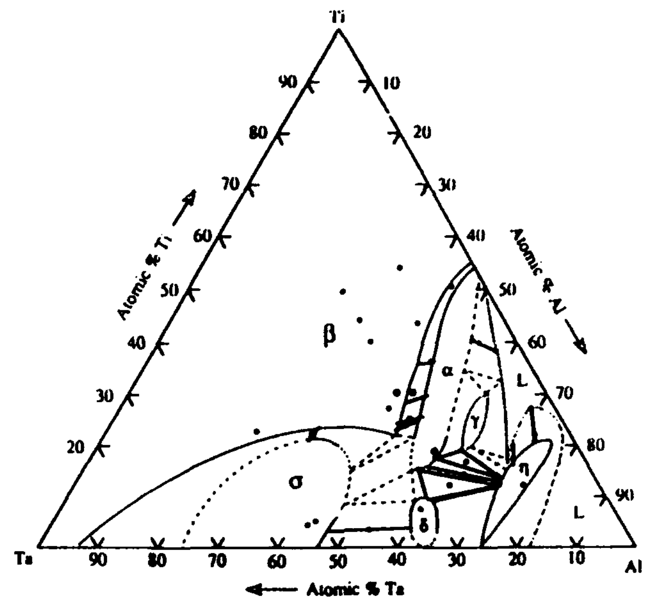
- Heavy segregation occurs upon solidification
- Large α & β phase fields at 1450°C
- Complex decomposition sequences -- corresponding large variation in microstructures and properties
- γ forms massively from α upon water quenching
- Phase boundary positions vary considerably with temperature -- indesirable from an applications standpoint

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Experimentally-Determined Ternary Ta-Ti-Al Isotherms



1350°C



1450°C

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SUMMARY

- RHC can be used to form full density intermetallics
- Natural composites can be formed by control of stoichiometry
- Artificial composites can be produced readily combining RHC with in-situ reactions.
- In-situ displacement reactions can be used to:
  1. Remove undesirable phases -- silica in $MoSi_2$
  2. Form dispersoid phases -- SiC in $MoSi_2$
  3. Form interface coatings

     Alumina in Al_3Nb/Nb and NiAl/Nb composites

     Refractory metal carbides in NiAl/W and NiAl/Mo composites
- Dual schemes (matrix enhancement vs. hybrid reinforcements) are required to achieve desirable low and high temperature properties.

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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Future Directions

RHC Processing

- Continue studies of alumina formation and matrix development in NiAl/Nb composites.
- Investigate the possibility of combining RHC, in-situ coating and fiber alignment.

$MoSi_2$ Matrix Composites

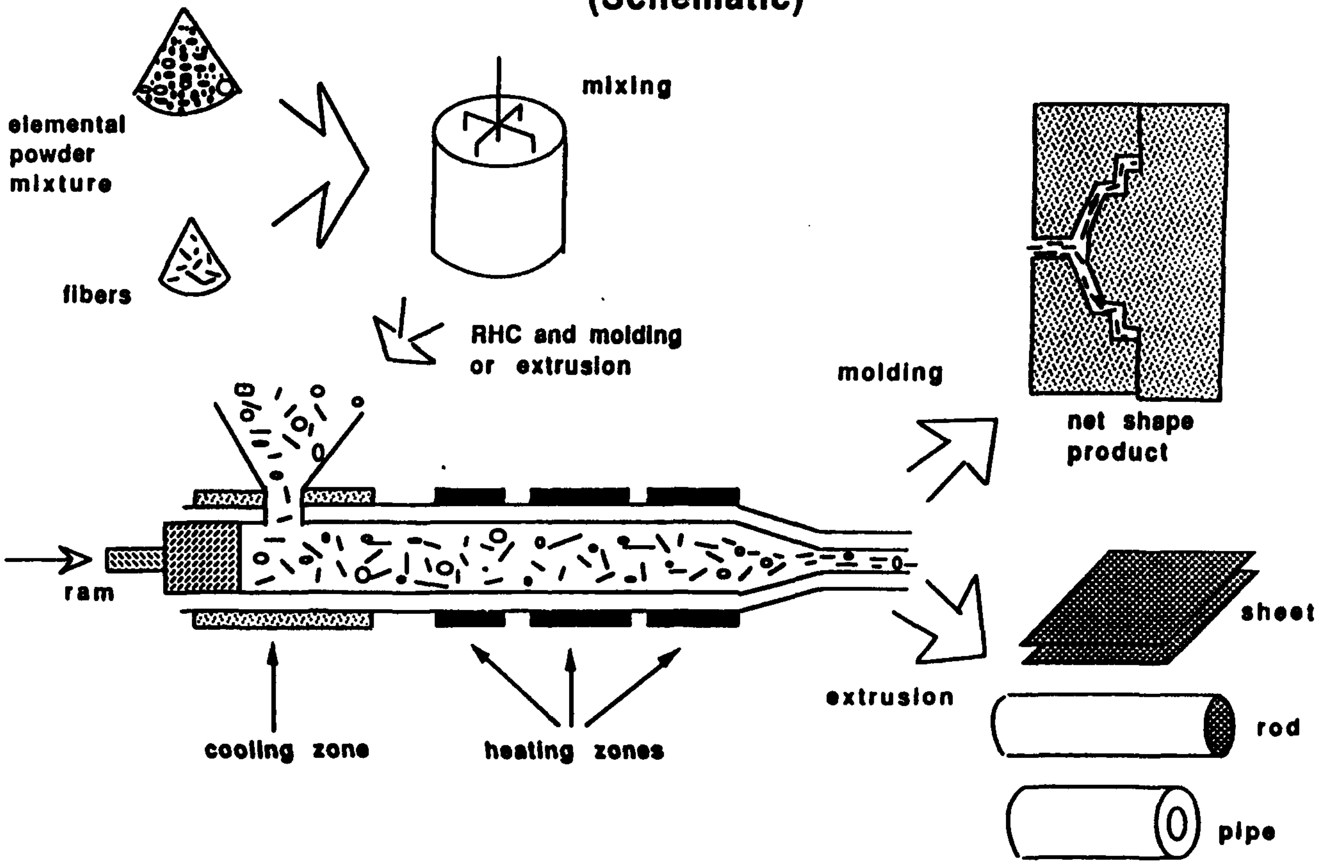
- Characterize the mechanical properties and environmental stability of enhanced silica-free matrices (vs. SiC content) -- origin of DBTT.
- Combine enhanced matrices with refractory metal toughening -- lower CTE mismatch and better creep strength?
- Complete phase equilibria studies in Mo-Si-C system.
- Develop of in-situ coating schemes to replace sol-gel approach (e.g., Si_3N_4).
- Investigate other in-situ formation sequences.
- Extend processing scheme to other silicide and silicide IMC systems.

NiAl Matrix Composites

- Characterize and optimize the properties of NiAl reinforced with in-situ coated Nb and SiC particulate at both room and elevated temperatures.
- Continue investigation of alternative schemes for interface modification in Mo, W and alumina-reinforced NiAl.

A Combination of RHC, In-Situ Coating and Fiber Alignment

(Schematic)



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CERAMIC COMPOSITES

Applications of Sol-Gel, Glass-Ceramics and Microwave Processing

D.E. Clark
D.C. Folz
A.D. Cozzi
Z. Fathi

PROGRAM OBJECTIVE

Develop alternative methods for processing advanced ceramics and composites with specific emphasis on microwave processing.

OUTLINE

Microwave Processing

Low Expansion Matrix Development

MICROWAVE PROCESSES INVESTIGATED

Sintering
Annealing (superconductors)
Self-Propogating High-Temperature Synthesis
Joining
Surface Modification
Crystallization

MATERIALS SYSTEMS INVESTIGATED

High-Purity Alumina - Sintering and Joining

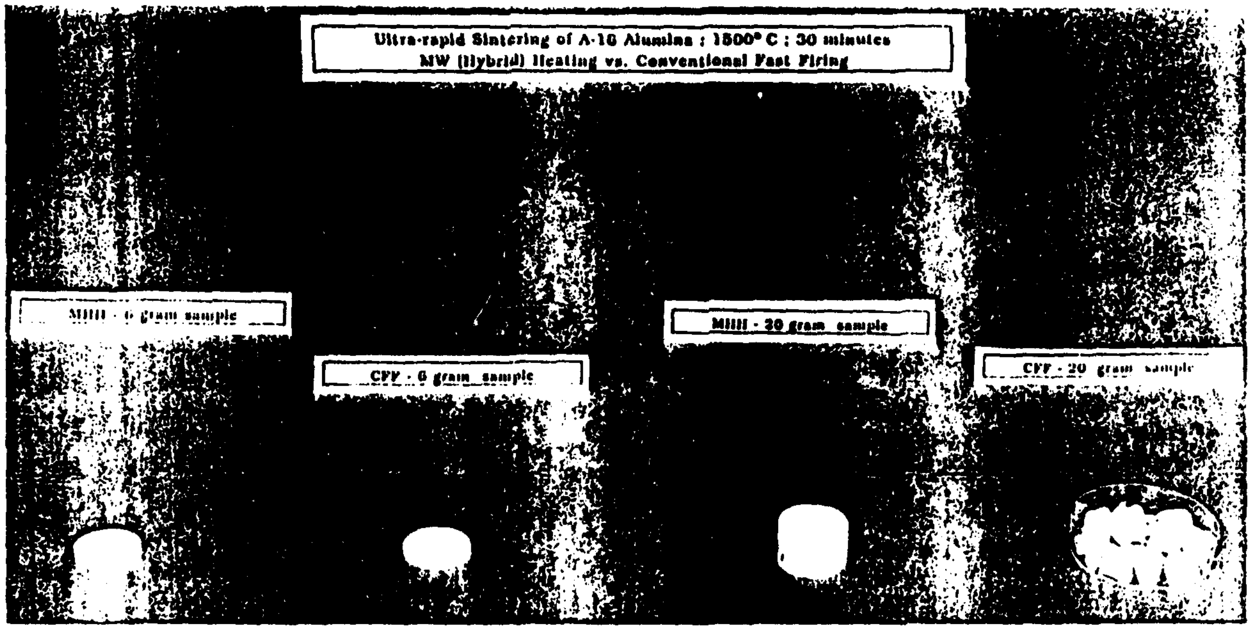
$YBa_2Cu_3O_{7-x}$ Superconductors - Sintering and Annealing

$\left.\begin{array}{c}TiC\\ Al_2O_3/TiC\\ Others\end{array}\right]$ Microwave SHS

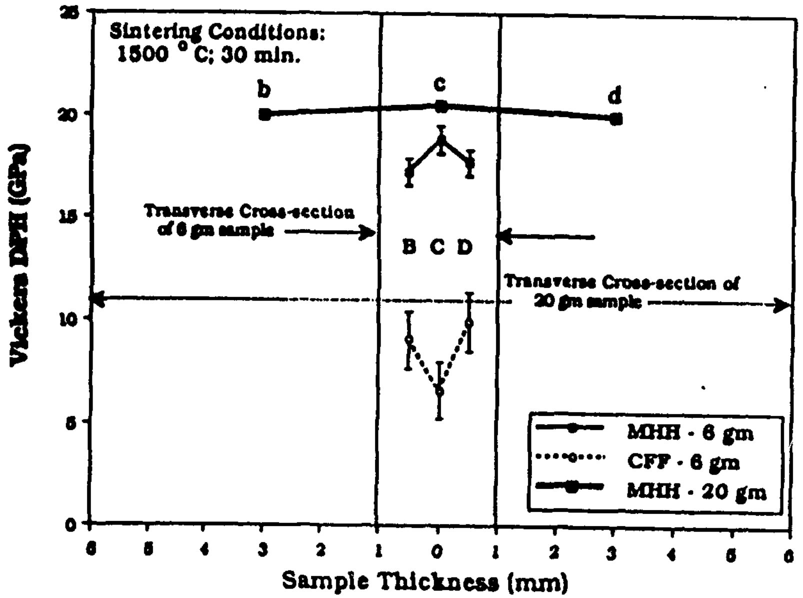
$Na_2O \cdot Al_2O_3 \cdot SiO_2$ - Surface Modification

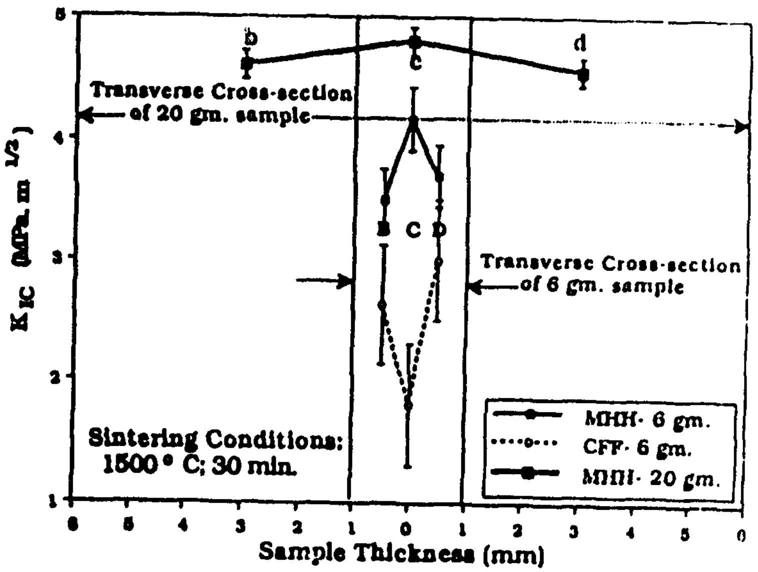
$\left.\begin{array}{c}Li_2O \cdot 2SiO_2\\ BaO \cdot Al_2O_3 \cdot 2SiO_2\end{array}\right]$ Crystallization

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

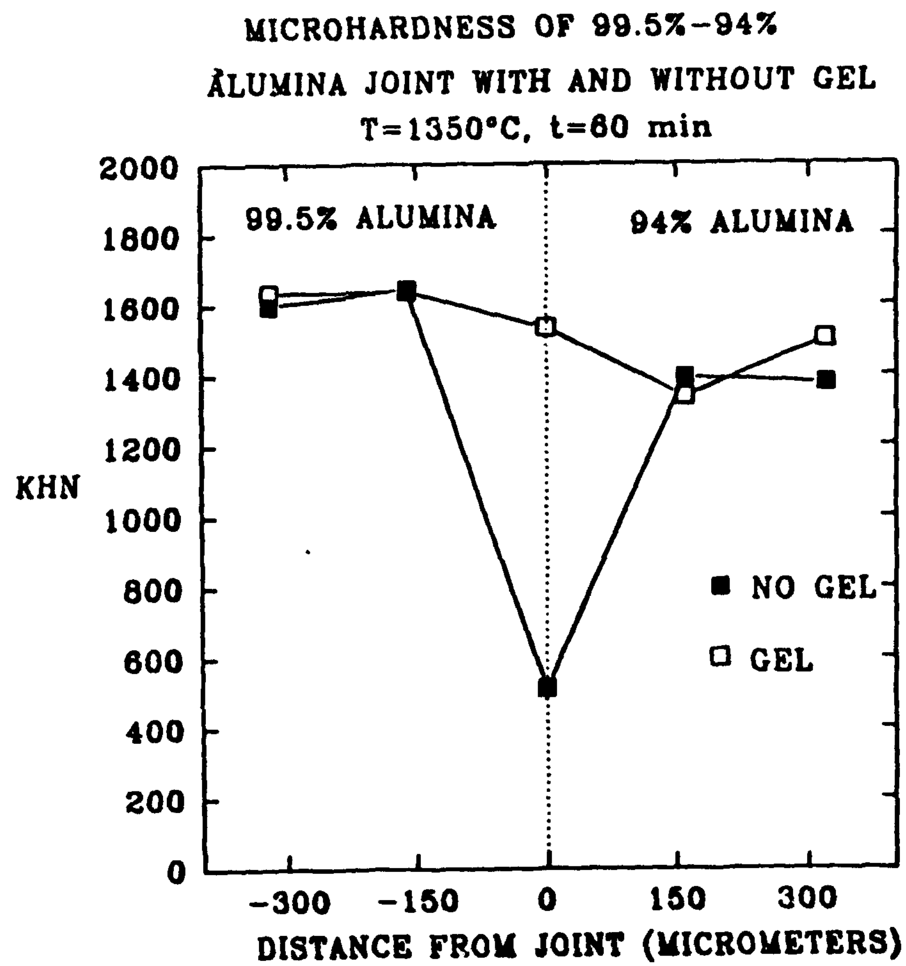


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

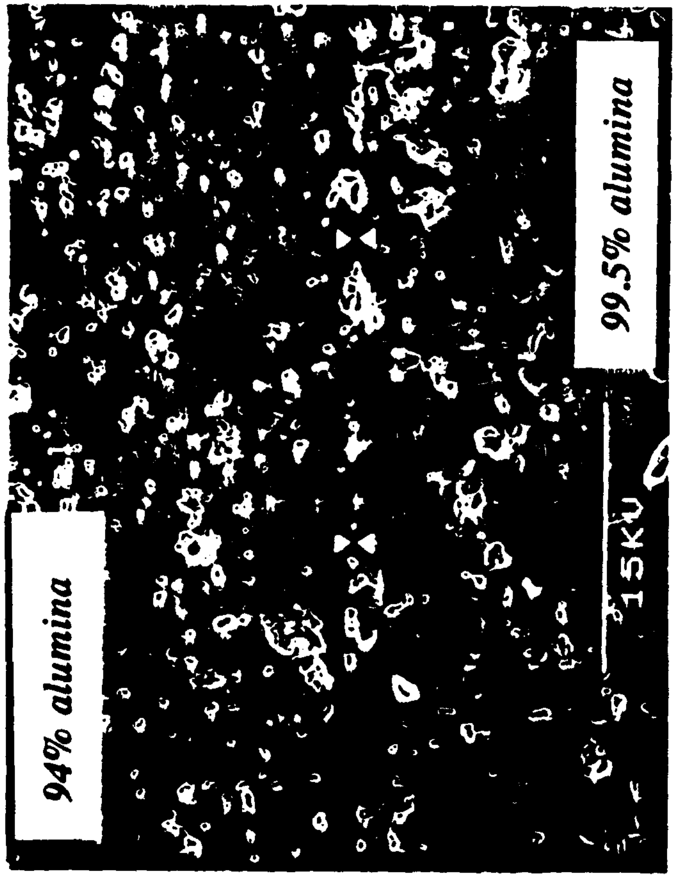


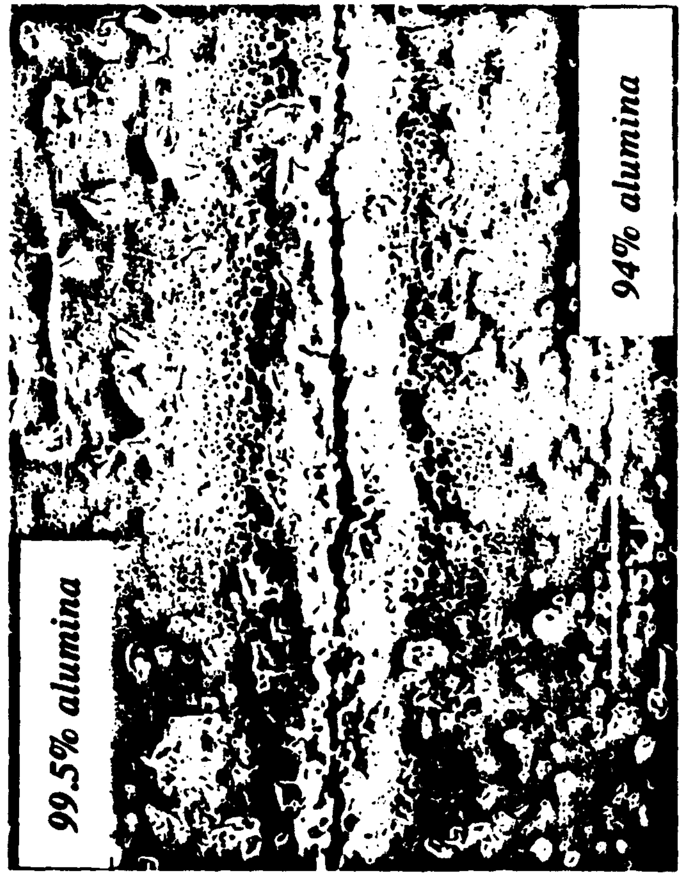


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

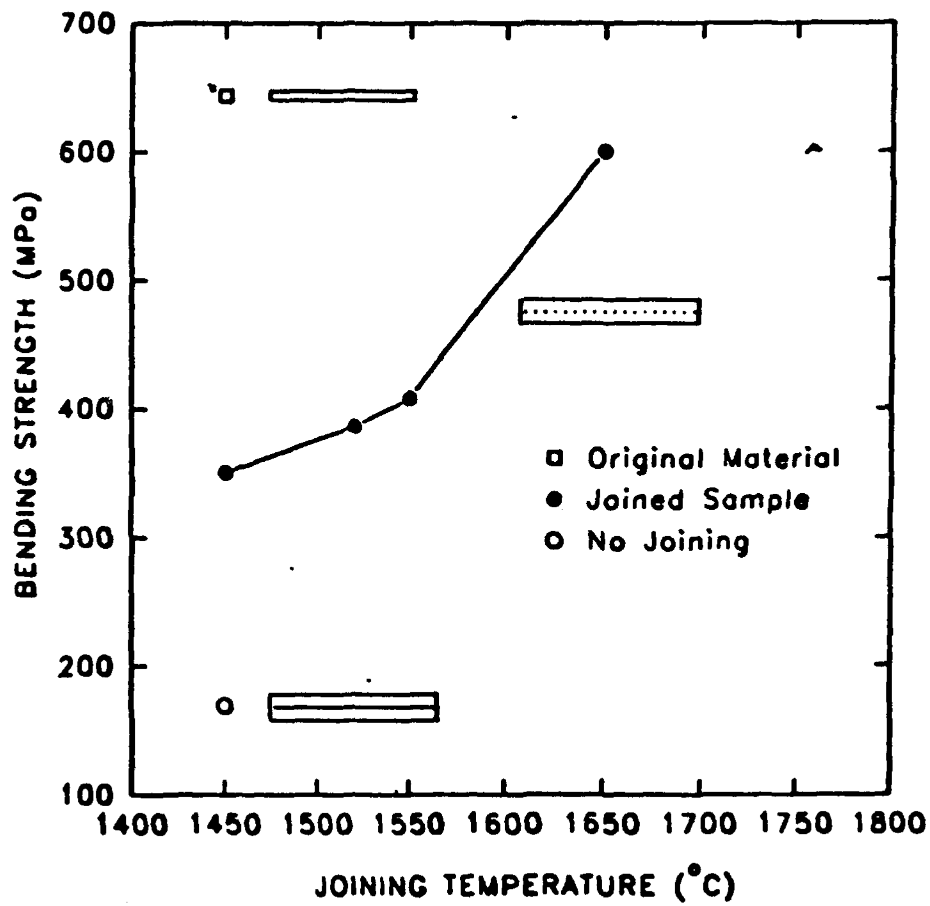




* 99.5%-GEL-94% ALUMINA
T=1350°C, t=60 min

* 99.5%-GEL-94% ALUMINA
T=1350°C, t=60 min

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



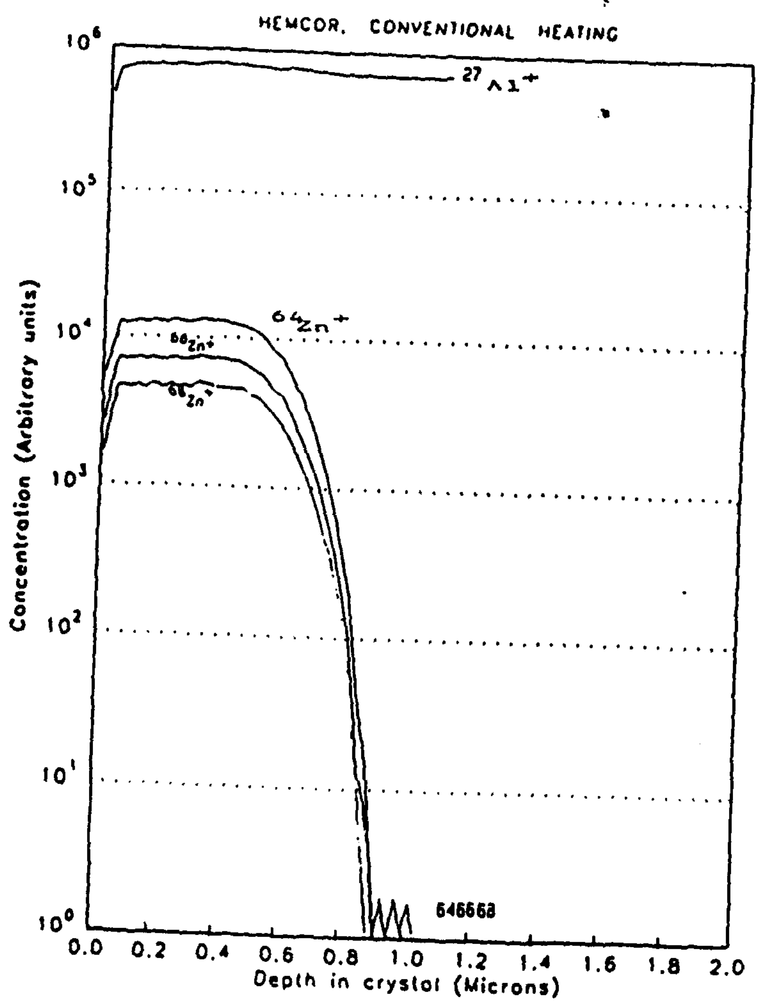
MICROWAVE CONTROLLED COMBUSTION SYNTHESIS (MICROCOM)

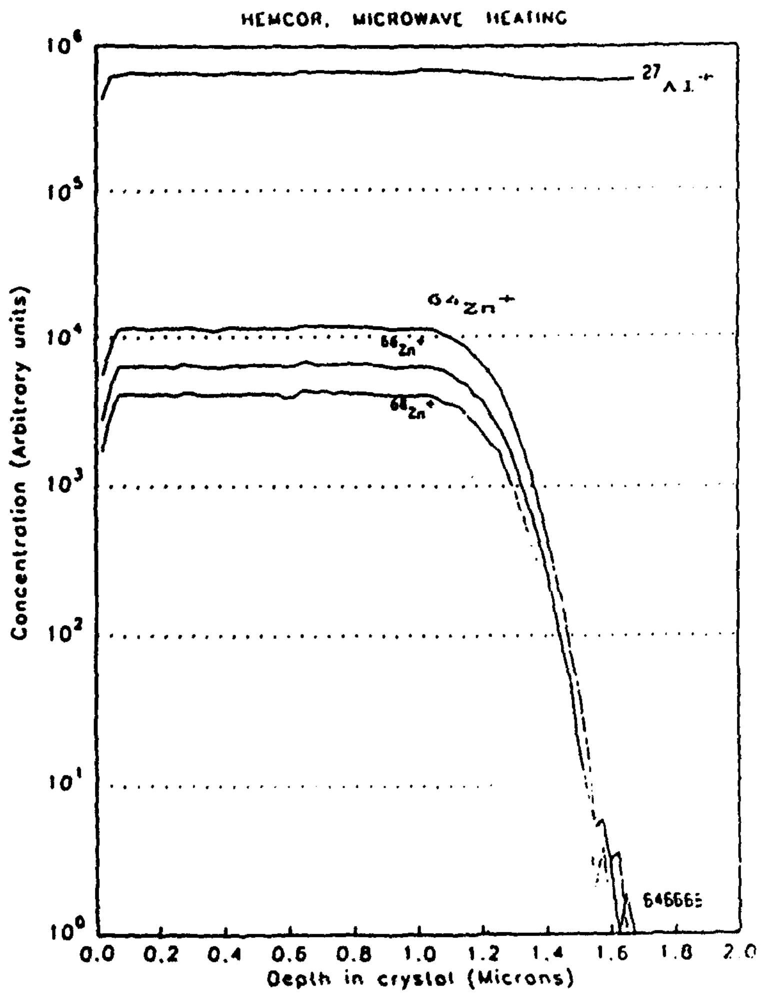
PROCESSING TIME:

0:00 min. 6:00 min. 8:00 min. 12:00 min.

Microwave ignition and controlled combustion synthesis (MICROCOM). The reacted volume increases with increasing exposure to microwave energy. When the microwave energy is turned off, the combustion reaction halts.

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS





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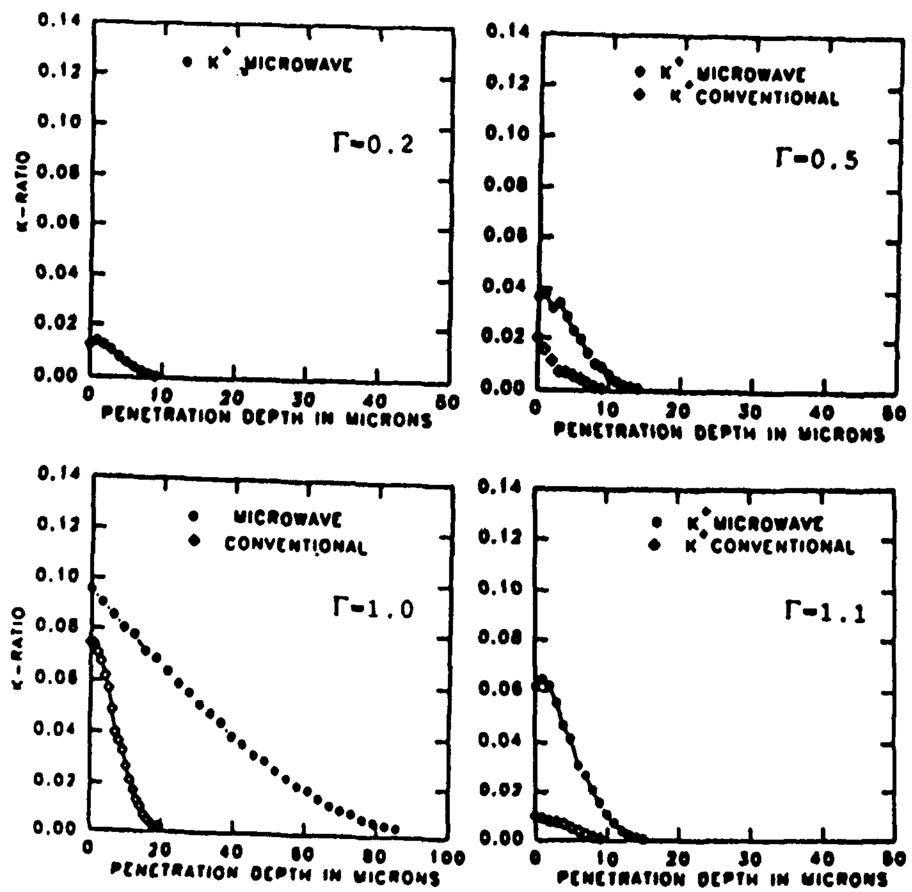
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



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LOW EXPANSION MATRIX DEVELOPMENT PROJECT GOALS

To evaluate $BaO \cdot Al_2O_3 \cdot 2SiO_2$ as a potential matrix material.

To investigate sol-gel as an alternative processing route to traditional glass-ceramic processing.

To investigate the use of microwave energy for processing composites.

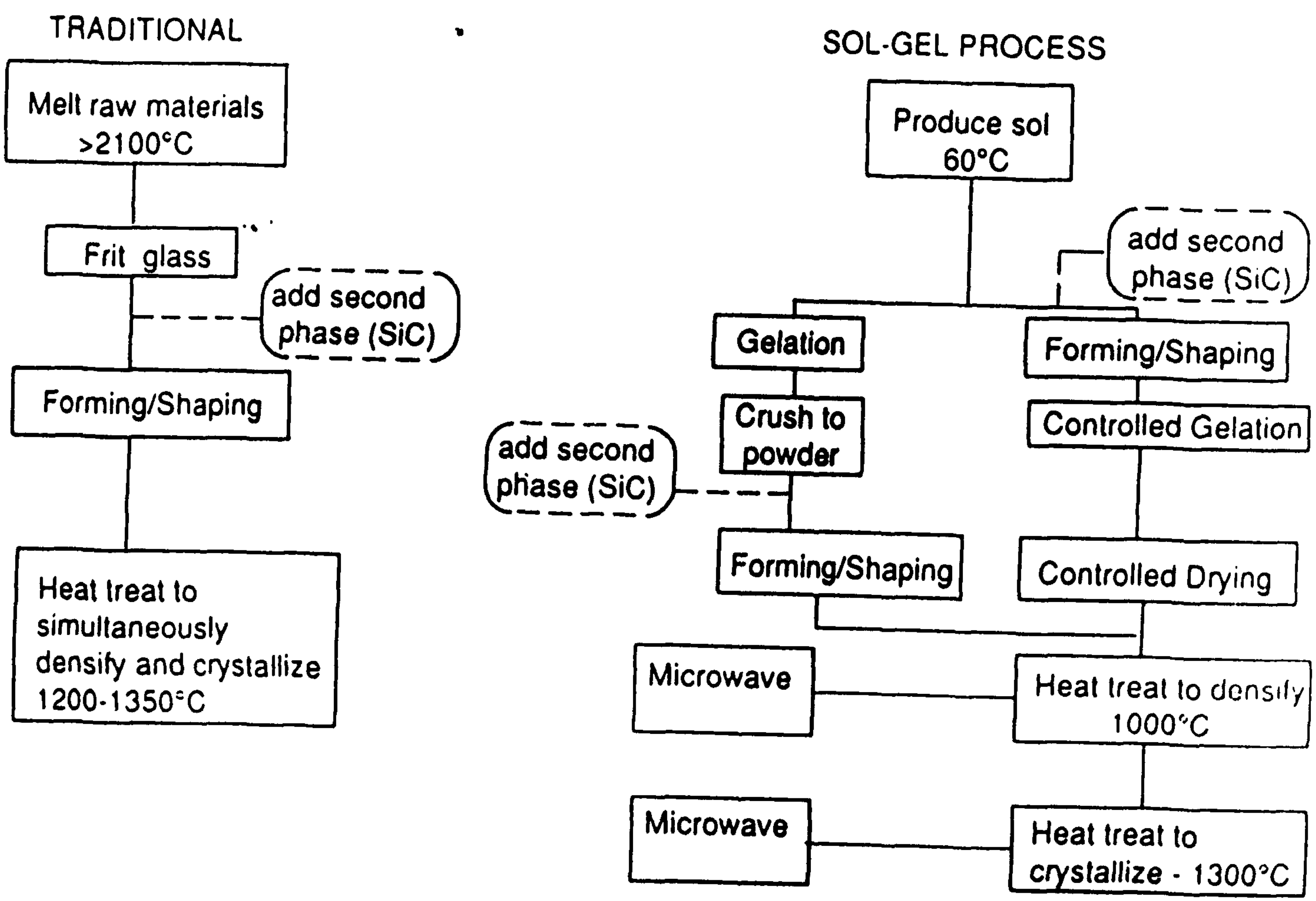
WHY CELSIAN?

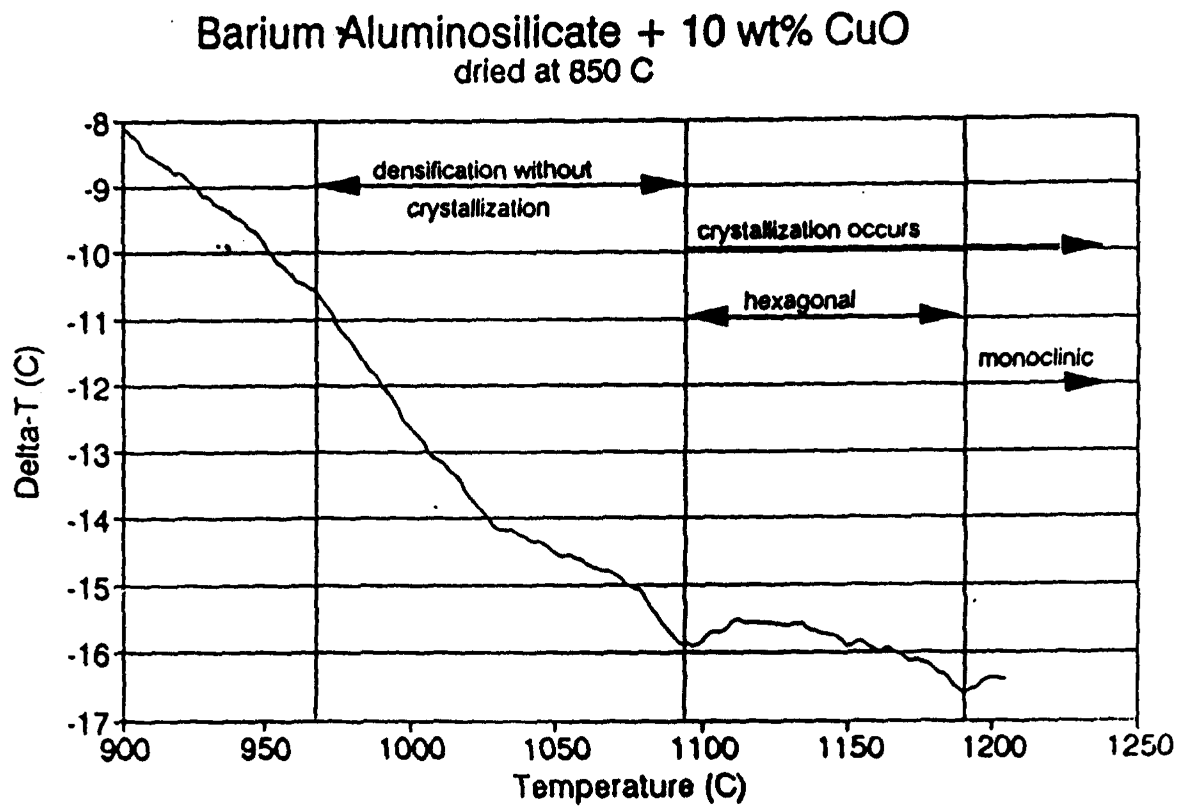
Celsian has several properties that make it attractive as a potential matrix material

- **CTE 2.3 x 10^{-6}/°C**
- **Celsian phase stable to 1590 °C**
- **Formability**
- **Oxidation resistant**
- **Compatible with SiC fibers**

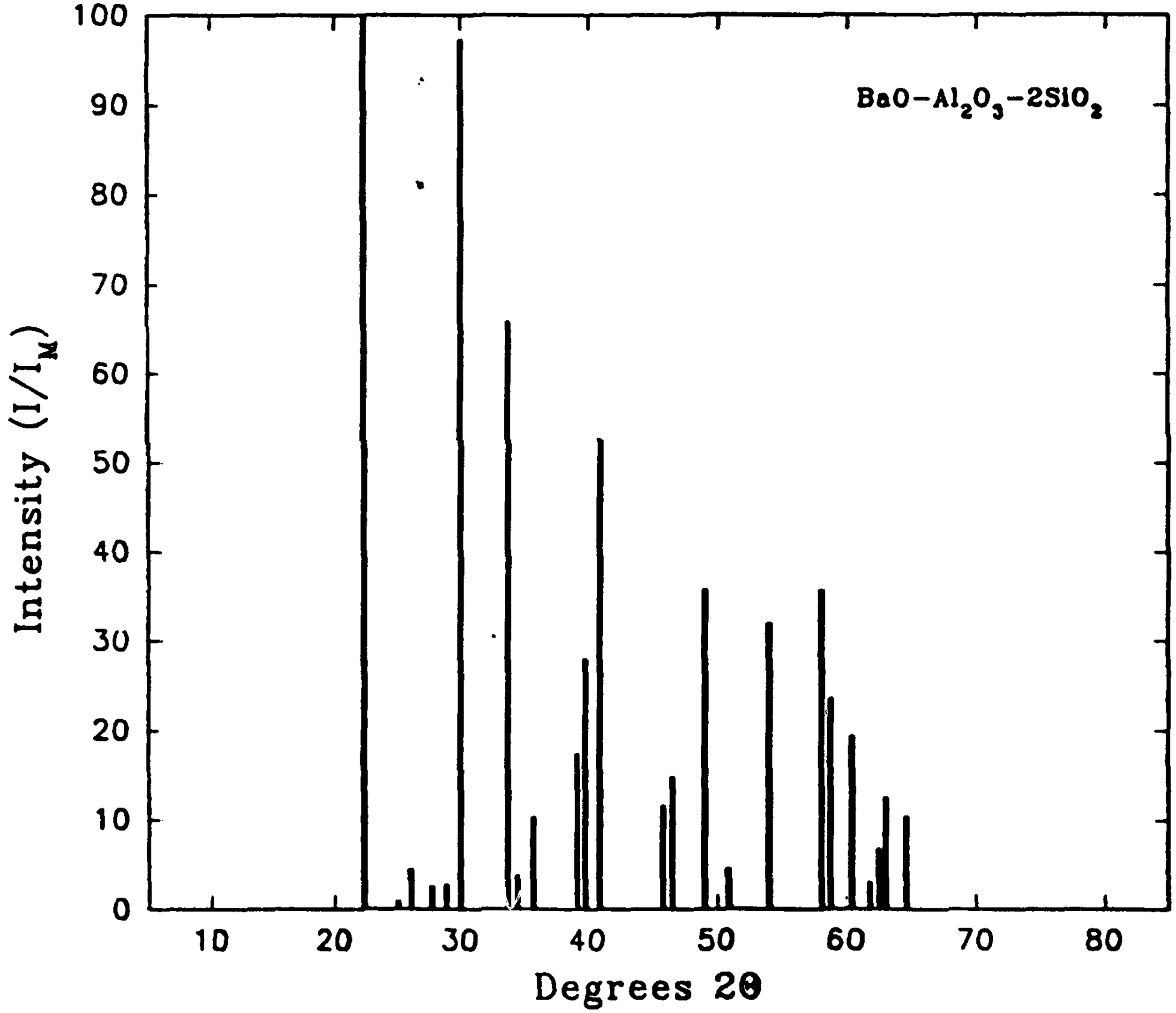
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

THE GLASS CERAMIC PROCESSING OF CELSIAN




Barium Aluminosilicate + 10 wt% CuO
dried at 850 C
densification without crystallization
crystallization occurs
hexagonal
monoclinic
Delta-T (C)
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
900
950
1000
1050
1100
1150
1200
1250
Temperature (C)

INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



All peaks correspond to the hexagonal phase

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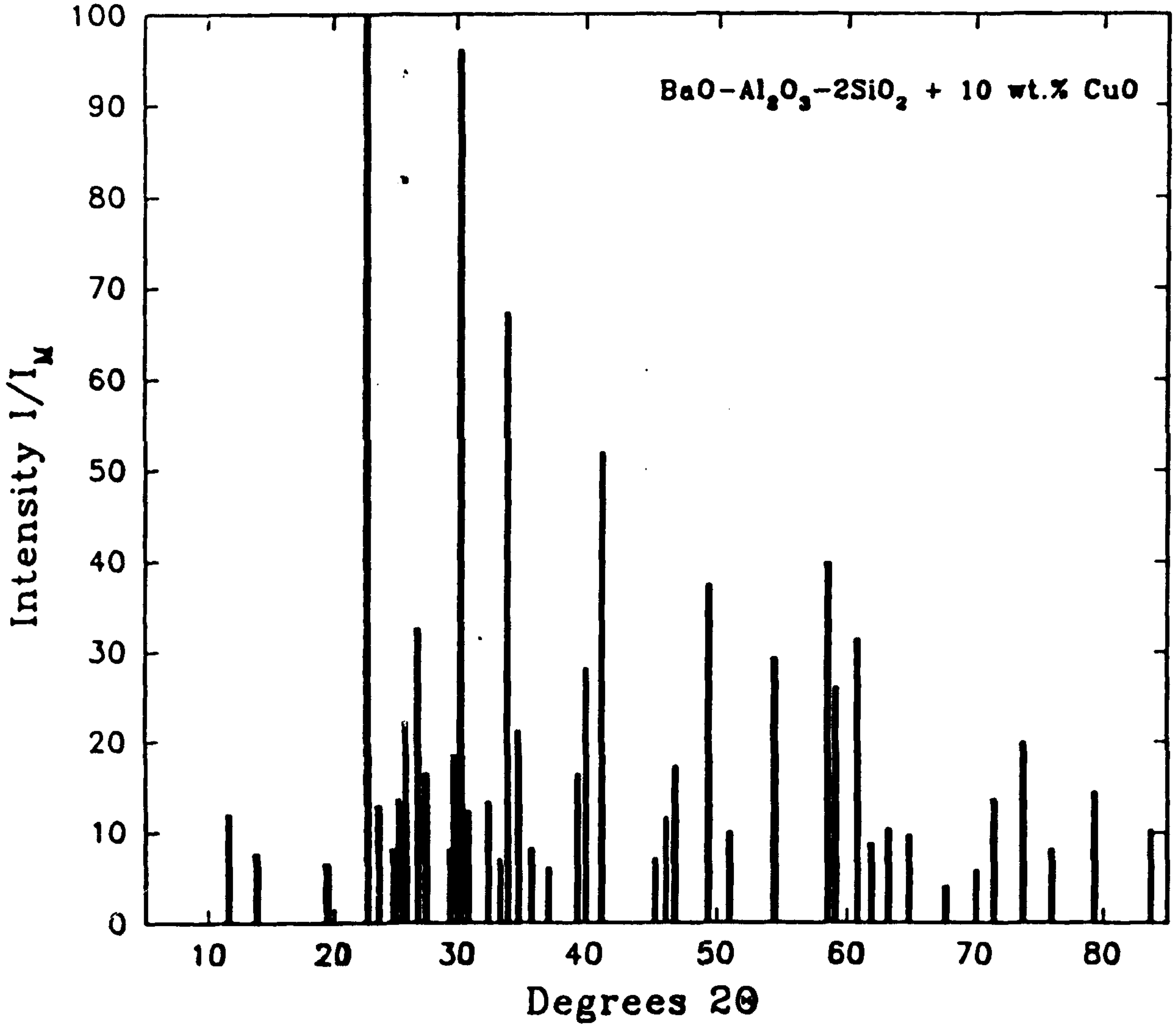
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



most peaks correspond to the monoclinic phase

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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

ACCOMPLISHMENTS

Sintering and annealing can be accomplished at lower temperatures and in less time.

Extremely rapid/uniform heating rates are possible without thermal shocking.

Better microstructural homogeneity and properties, and this improves even more with scale-up.

SHS reactions involving powders can be performed efficiently in the microwave. In some systems, SHS of shaped powders can be controlled with the potential for fabricating Functionally Gradient Materials (FGMs).

With the combined use of sol-gel processing, ceramics can be joined efficiently using microwave energy.

Surfaces can be modified to greater depths in shorter times in the microwave oven. Also of importance, the chemical profiles can be tailored (in systems studied) to improve the mechanical properties.

Crystallization can be performed at lower temperatures in the microwave oven.

ACCOMPLISHMENTS cont.

Produced amorphous $BaO \cdot Al_2O_3 \cdot 2SiO_2$ glass using two different sol-gel routes.

Determined the processing temperatures for densification and crystallization.

Evaluated CuO as a microwave-absorbing additive to facilitate the crystallizatin of celsian.

Crystallized samples using microwave hybrid heating and stand-alone microwave energy.

FUTURE WORK

Fabricate composites using both hybrid and stand-alone microwave heating.

Evaluate microwave-transparent matrix materials reinforced with

- microwave-absorbing SiC fibers
- microwave-transparent mullite fibers
- transparent and absorbing fibers with microwave-tailored coatings (i.e., CVD and sol-gel).

Pursue work proposed to other agencies to investigate fundamentals of microwave/materials interactions.

PROCESSING OF CERAMIC-MATRIX COMPOSITES

Principal Investigator: M.D. Sacks

PROCESSING OF CERAMIC-MATRIX COMPOSITES

- FIBER DEVELOPMENT
- MATRIX DEVELOPMENT
- COMPOSITE FABRICATION

Approaches

- Viscous Processing
- Infiltration Processing

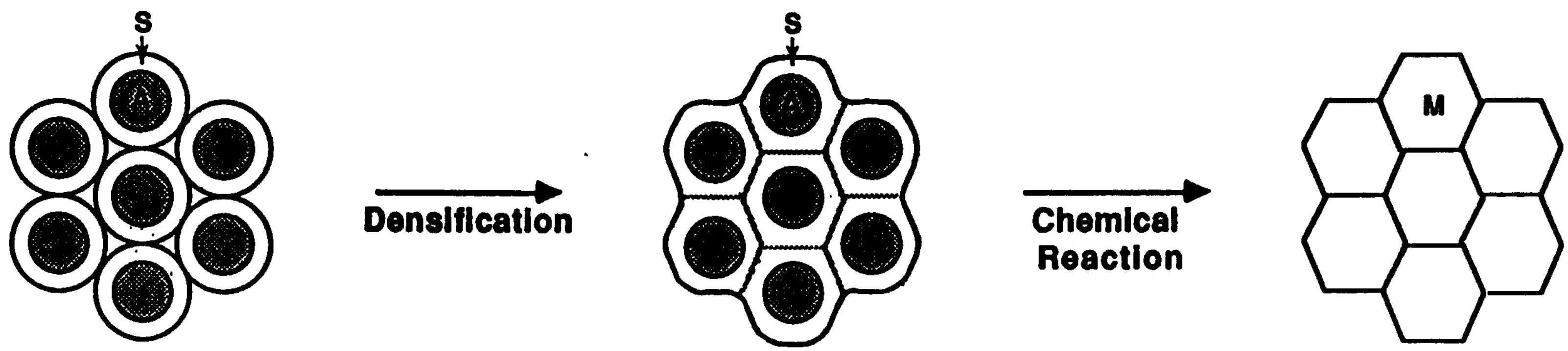
Potential Advantages

- Near Net Shape Fabrication
- High Relative Density (Low Porosity)
- Low Processing Temperatures

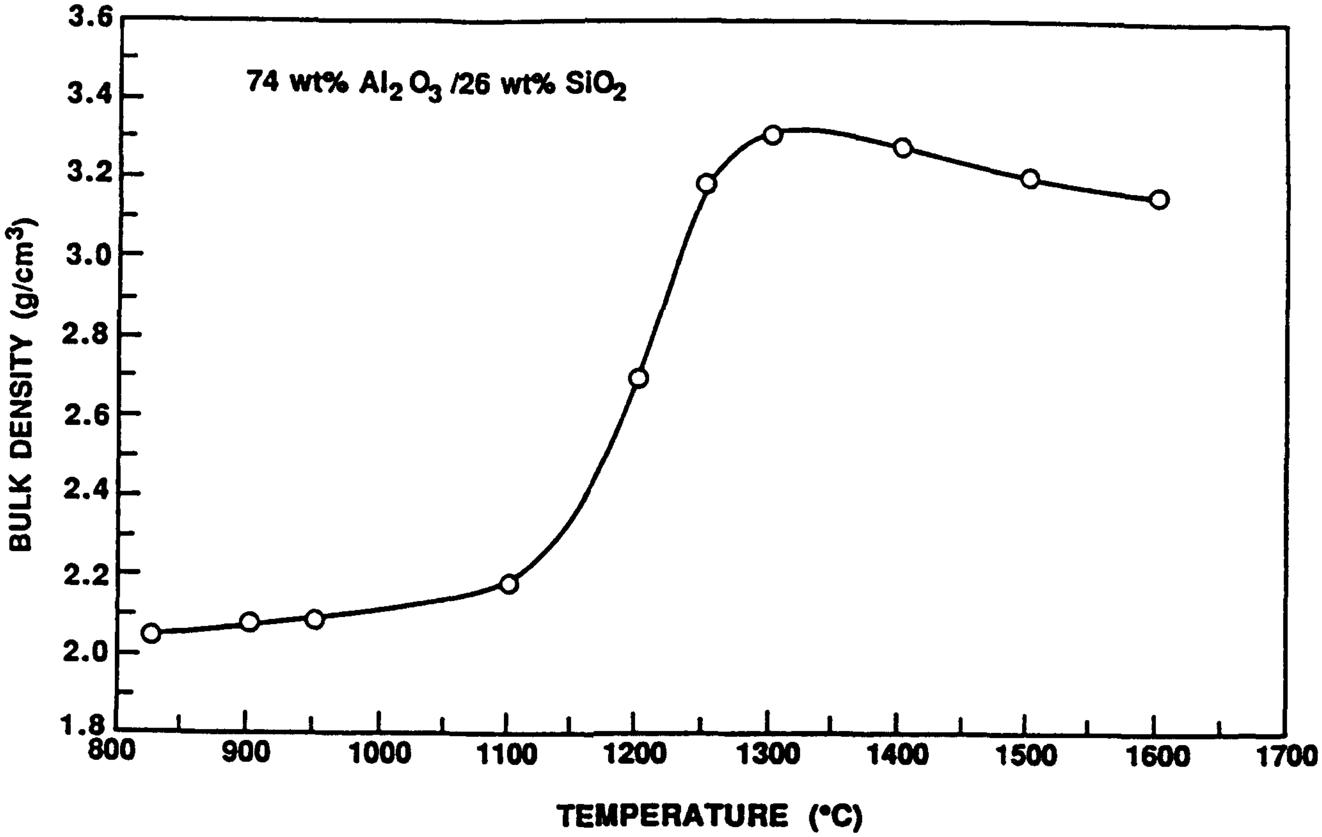
TRANSIENT VISCOUS SINTERING AND PRESSURE-ASSISTED TRANSIENT VISCOUS SINTERING

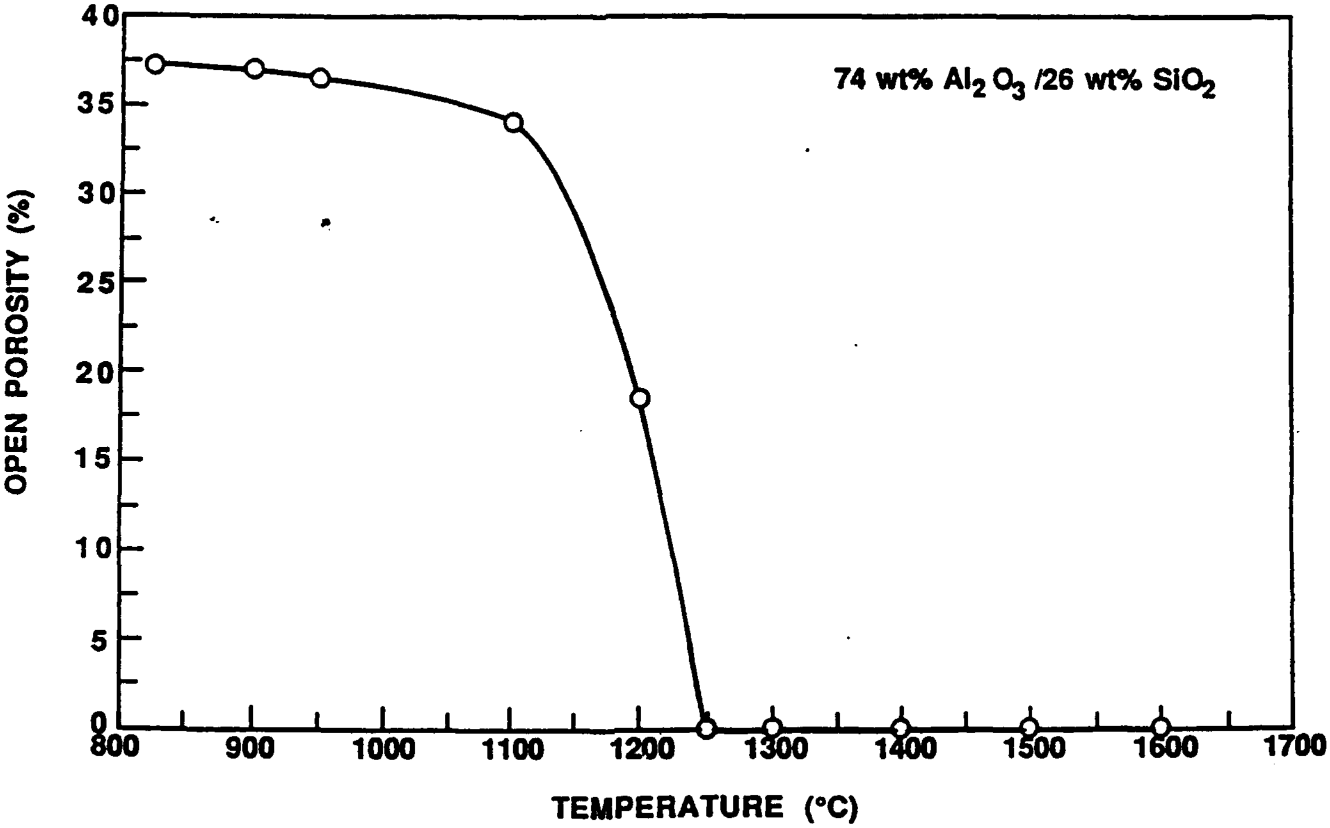
Consolidation of "microcomposite" powders by viscous deformation (with or without applied pressure) and subsequent tranformation (partially or completely) to a crystalline ceramic.

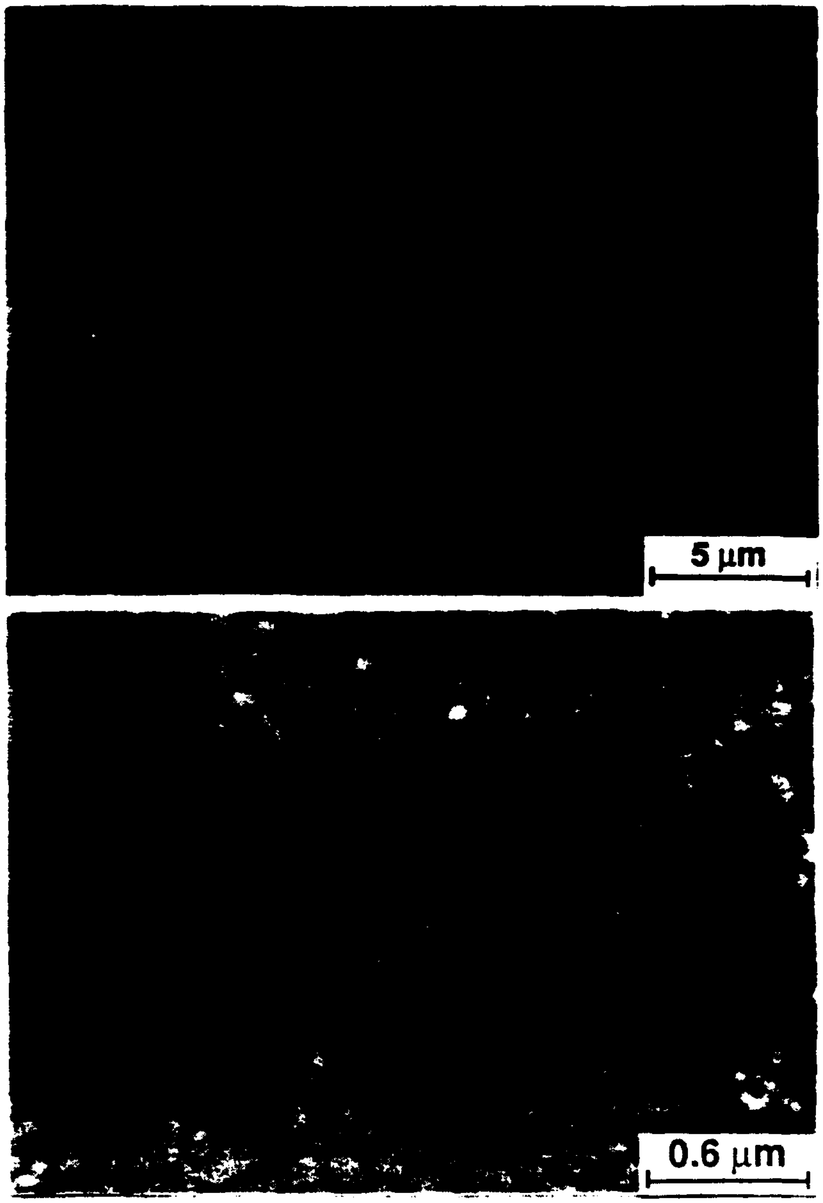
Transient Viscous Sintering of Mullite

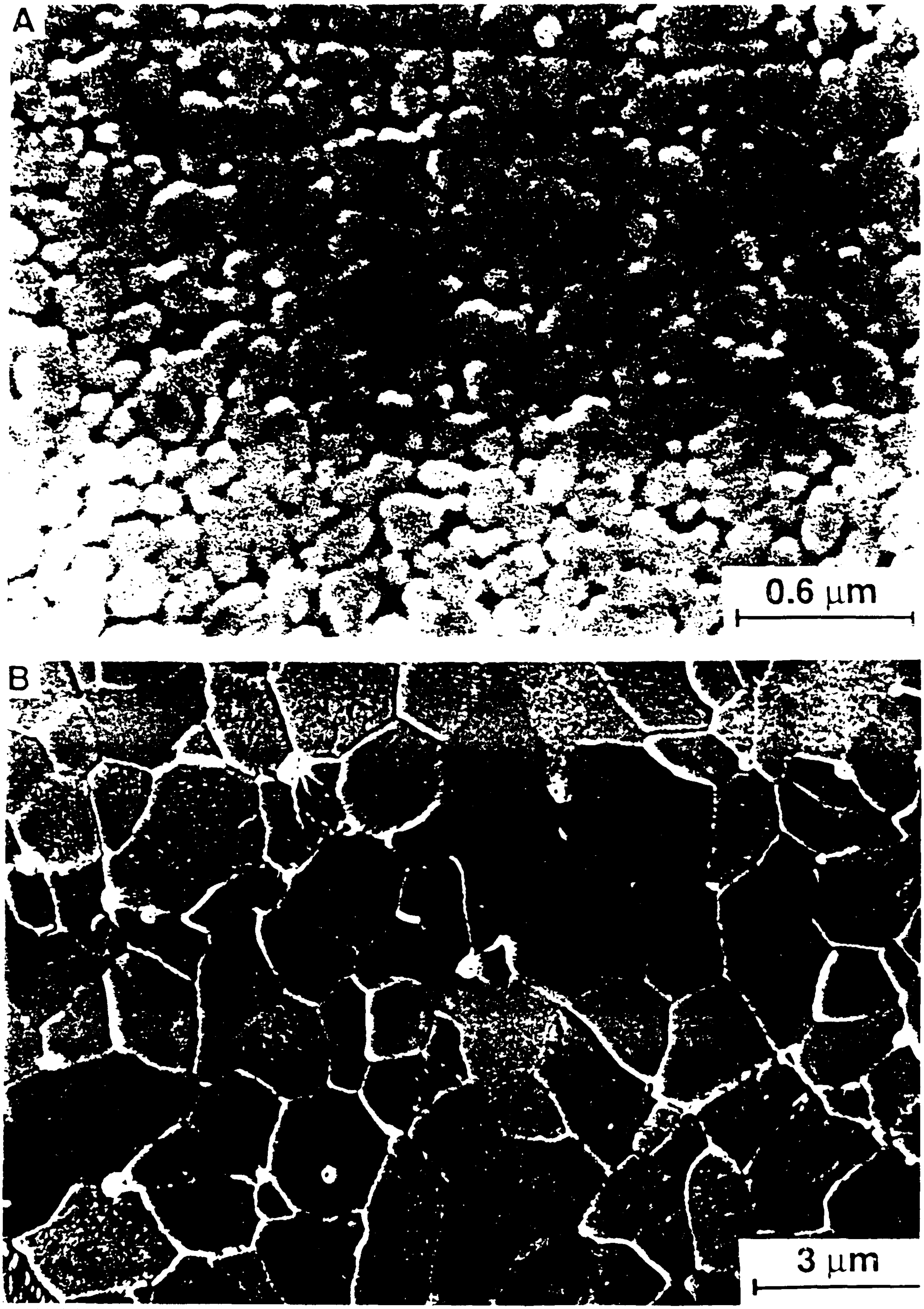


$$3Al_2O_3 + 2SiO_2 \longrightarrow 3Al_2O_3 + 2SiO_2 \longrightarrow 3Al_2O_3 \cdot 2SiO_2 \quad \text{(Mullite)}$$

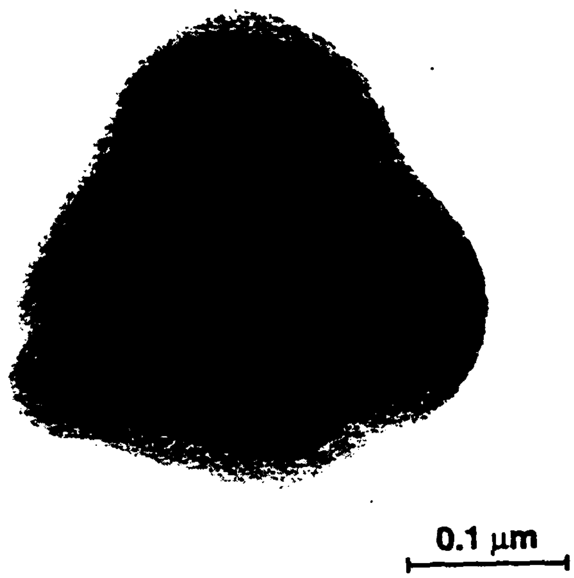

74 wt% Al_2O_3/26 wt% SiO_2
BULK DENSITY (g/cm³)
TEMPERATURE (°C)
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
800
900
1000
1100
1200
1300
1400
1500
1600
1700

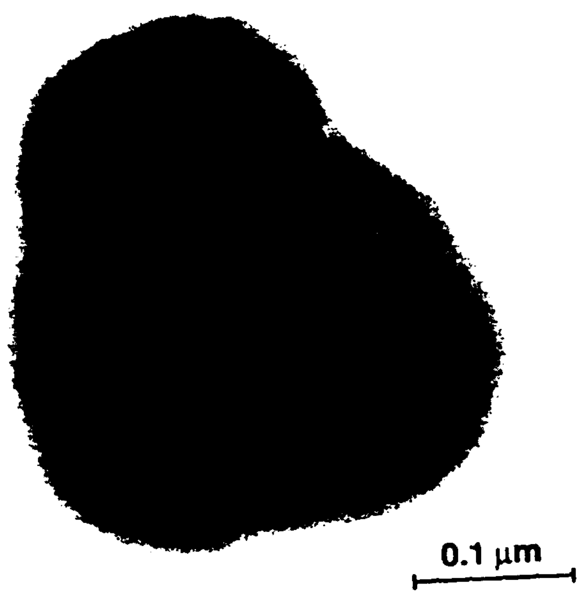

74 wt% Al_2O_3/26 wt% SiO_2
OPEN POROSITY (%)
TEMPERATURE (°C)
40
35
30
25
20
15
10
5
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700


5 μm
0.6 μm

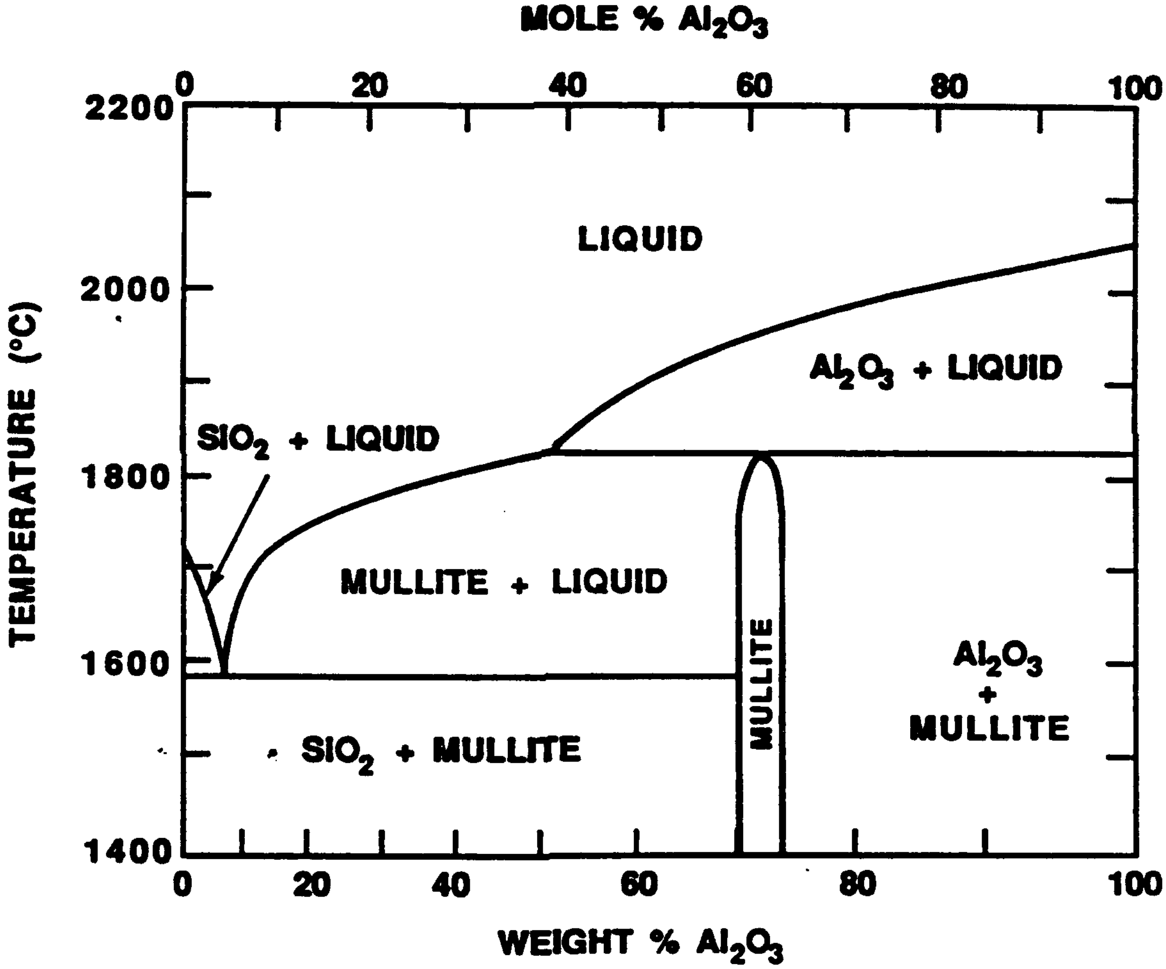

A
0.6 μm
B
3 μm


0.1 µm

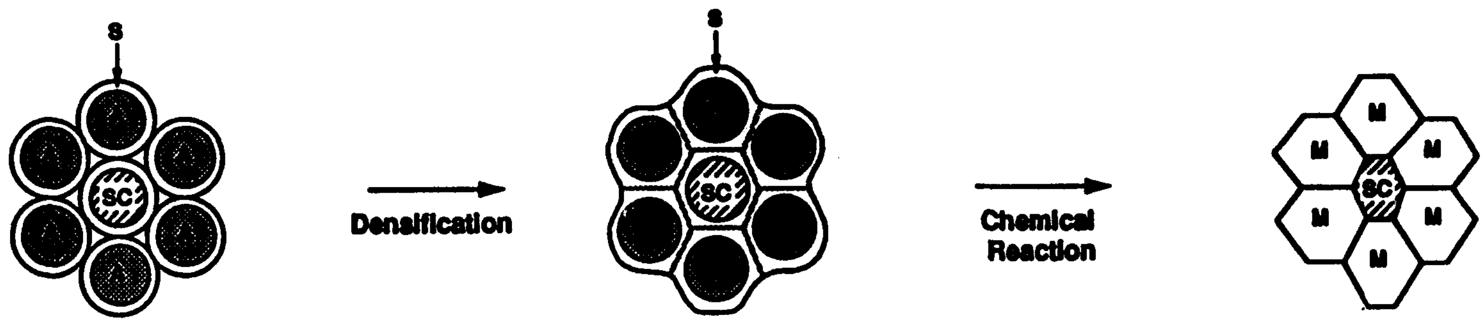

0.1 µm


0.1 µm

SiO_2 - Al_2O_3 PHASE DIAGRAM

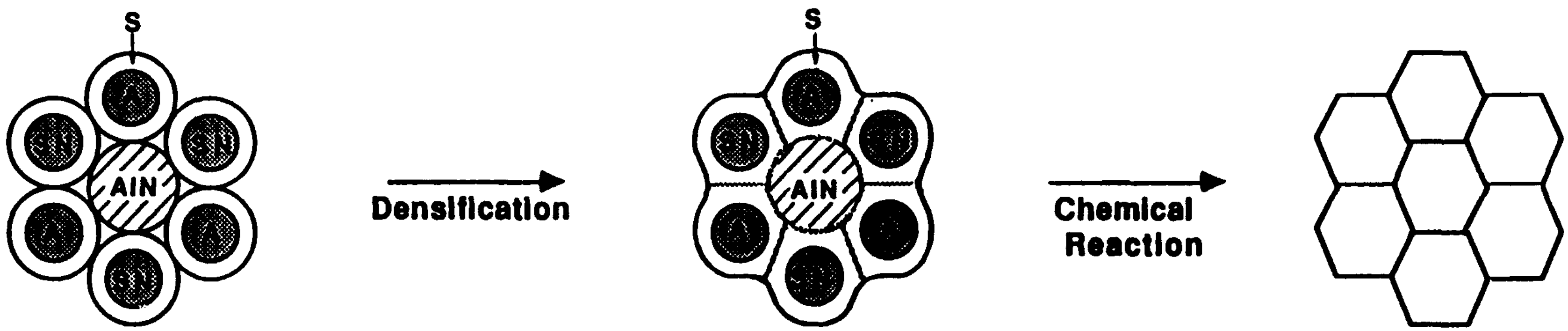


FABRICATION OF MULLITE/SILICON CARBIDE COMPOSITES

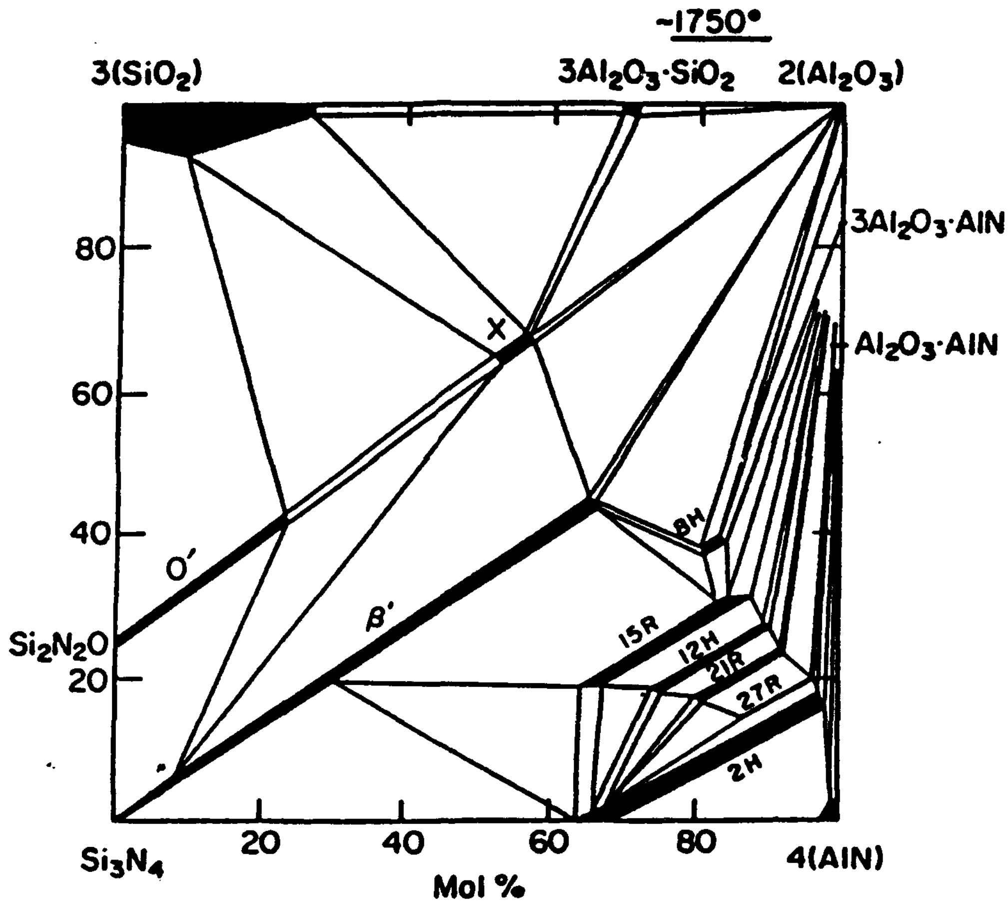


$$3Al_2O_3 + 2SiO_2 + xSiC \longrightarrow 3Al_2O_3 + 2SiO_2 + xSiC \longrightarrow 3Al_2O_3 \cdot 2SiO_2\ (\text{Mullite}) + xSiC$$

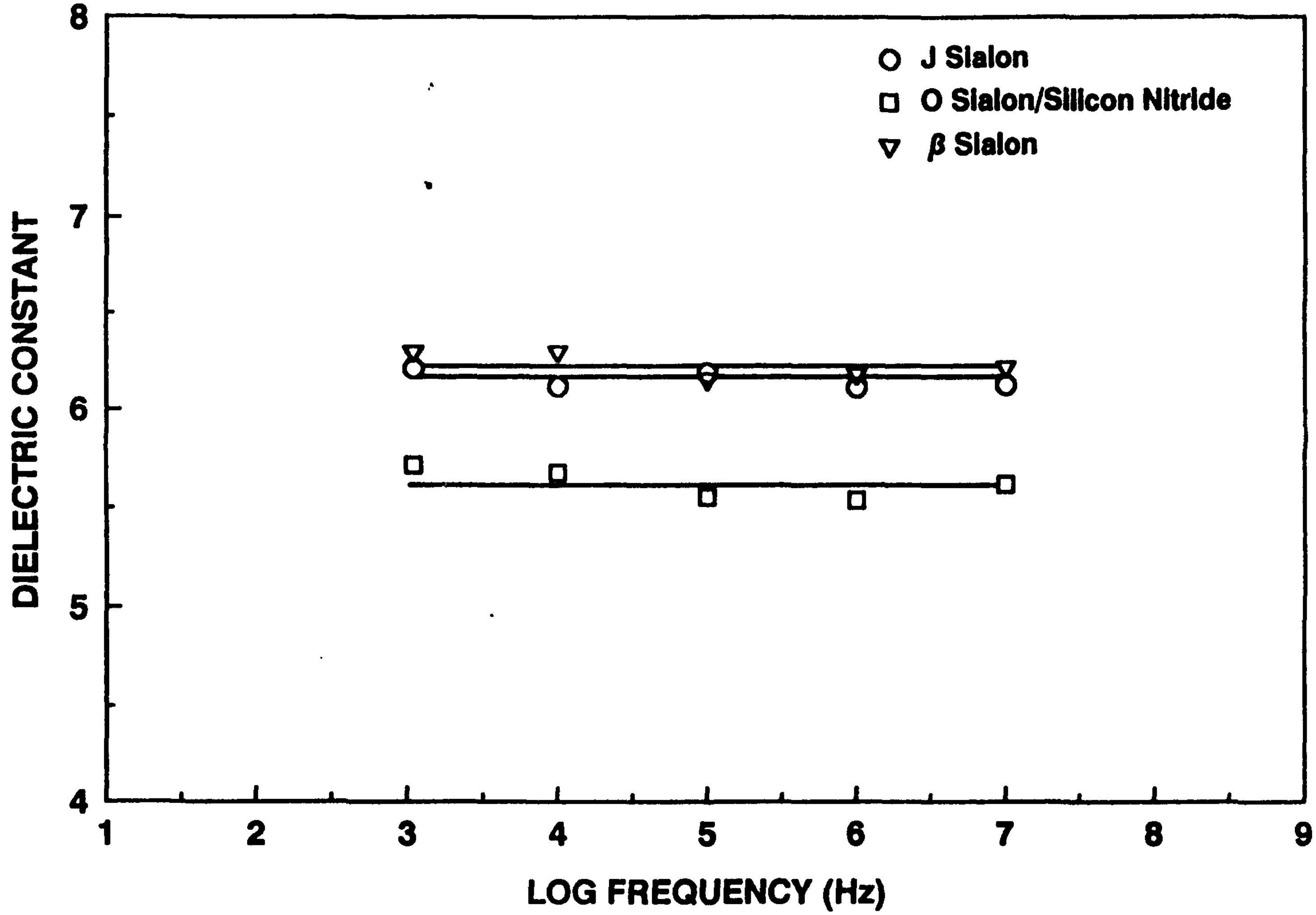
TRANSIENT VISCOUS SINTERING



$SiO_2 + Si_3N_4 + Al_2O_3 + AlN \longrightarrow SiO_2 + Si_3N_4 + Al_2O_3 + AlN \longrightarrow$ SIALON



~1750°
3(SiO2)
3Al2O3·SiO2
2(Al2O3)
3Al2O3·AlN
Al2O3·AlN
80
60
40
20
X
O'
Si2N2O
β'
8H
15R
12H
21R
27R
2H
Si3N4
20
40
60
80
4(AlN)
Mol %



J Sialon
O Sialon/Silicon Nitride
β Sialon
DIELECTRIC CONSTANT
LOG FREQUENCY (Hz)
8
7
6
5
4
1
2
3
4
5
6
7
8
9

CERAMICS AND COMPOSITES PREPARED BY VISCOUS AND TRANSIENT VISCOUS SINTERING OF SILICA-COATED PARTICLES

MULLITE

SILICA/ALUMINA

MULLITE/ALUMINA

MULLITE/SILICA

MULLITE/ZIRCONIA

MULLITE/SILICON CARBIDE PARTICLES

MULLITE/SILICON CARBIDE WHISKERS

SILICA/SILICON NITRIDE

SIALON (β, O, J PHASES)

SIALON/ALUMINA

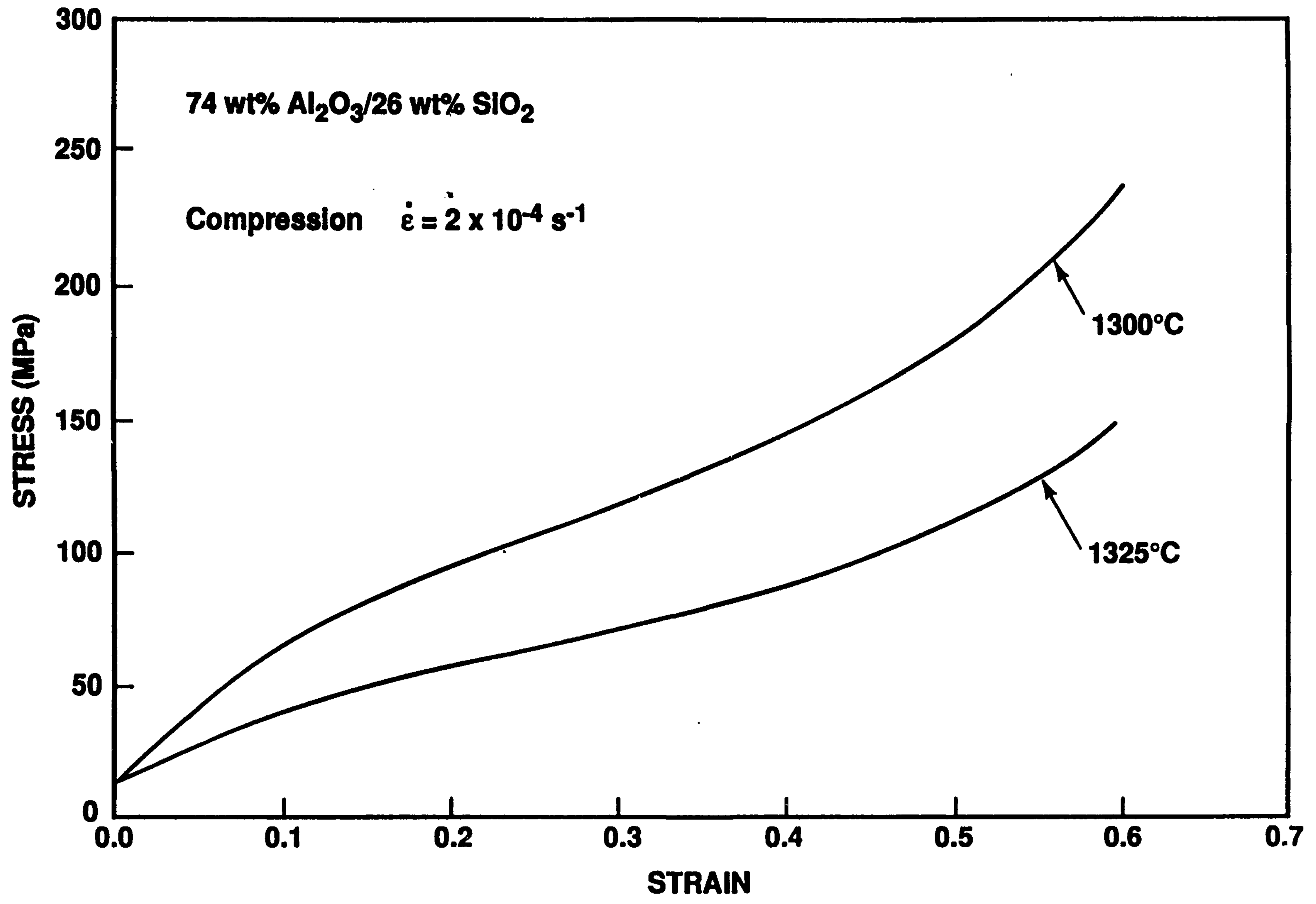
SIALON/SILICON NITRIDE

Recent Developments in Viscous Processing

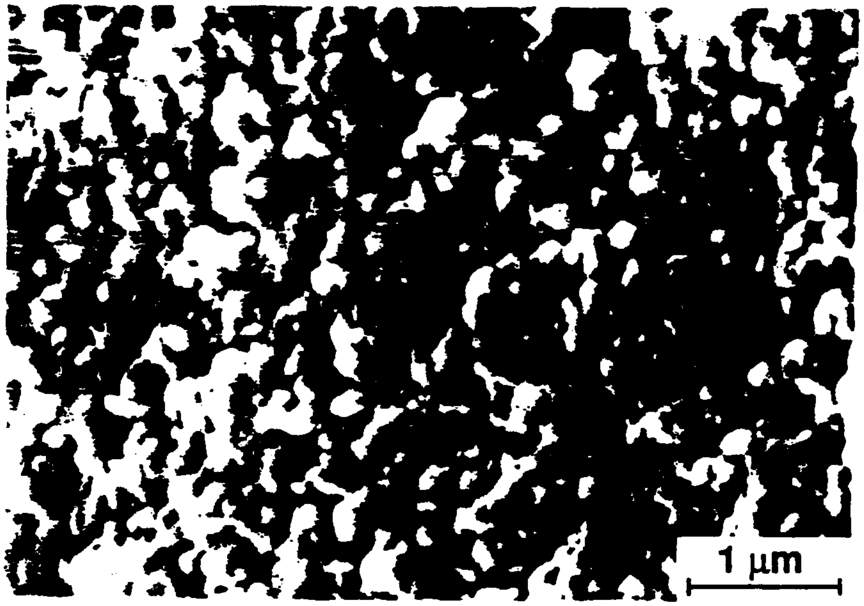
- **Pressure-Assisted Transient Viscous Sintering (PATVS)**
  (fiber-reinforced composites)

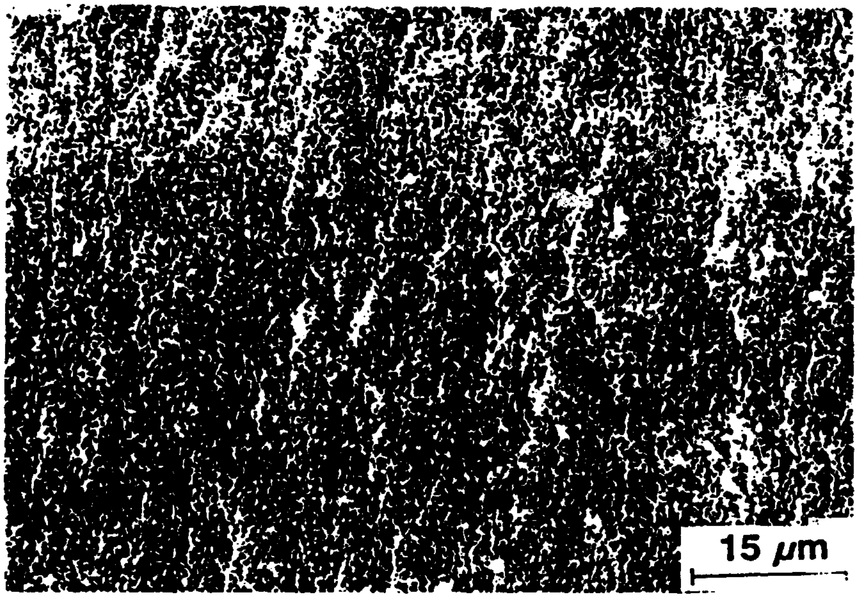
- **Seeded Phase Transformations**
  (lower processing temperatures, finer-grain microstructures)

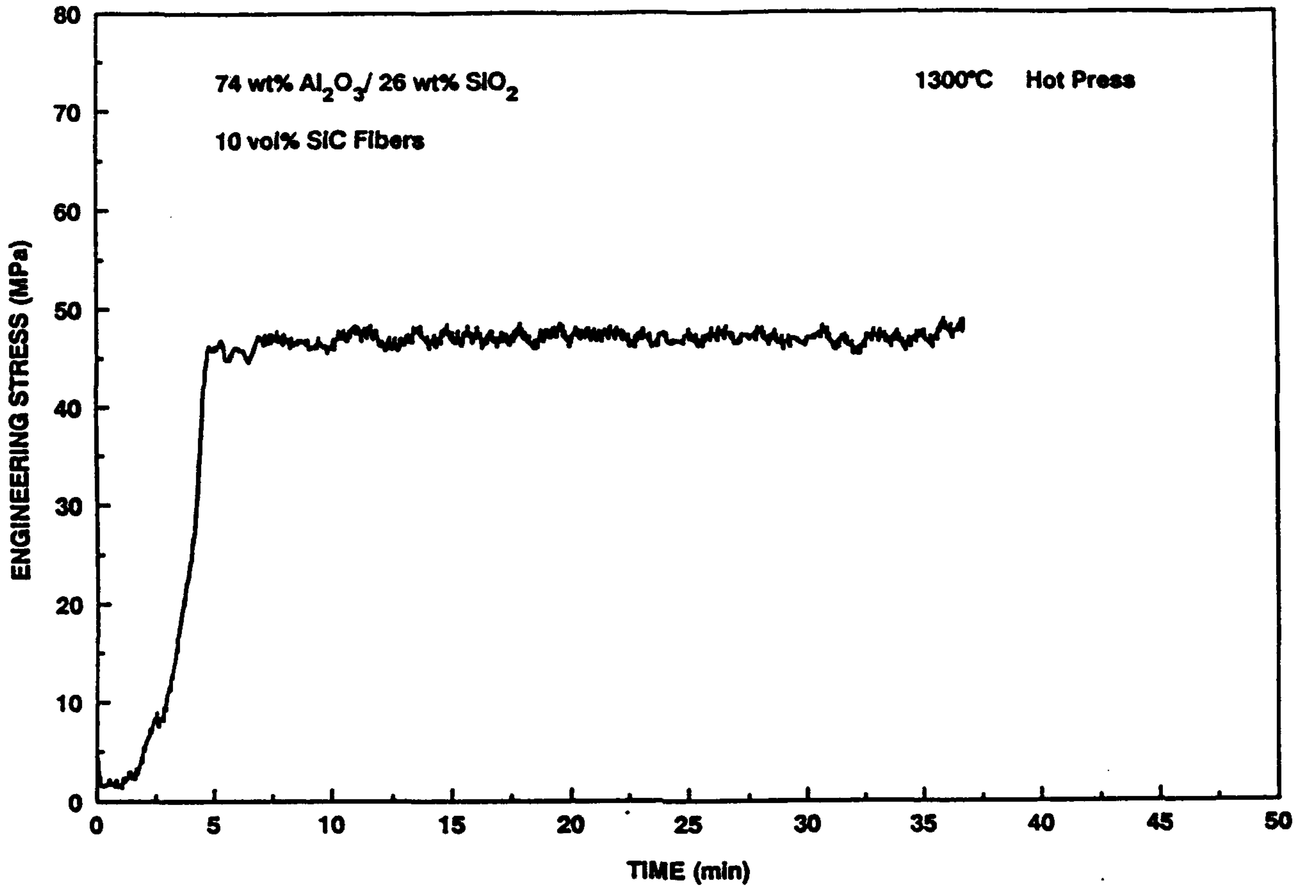
- **Microcomposite Particles with Multicomponent Coatings**
  (expanded range of compositions, lower processing temperatures)

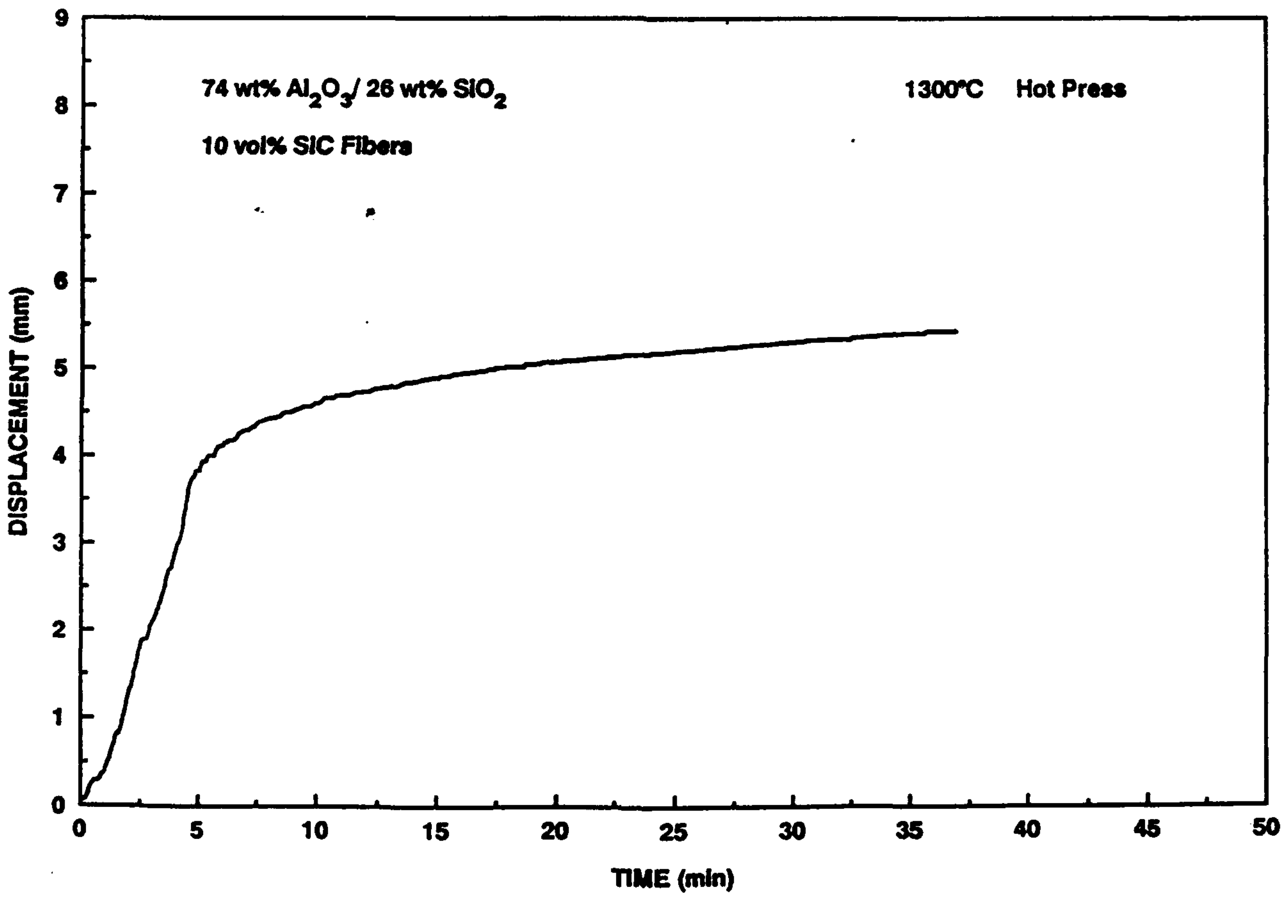


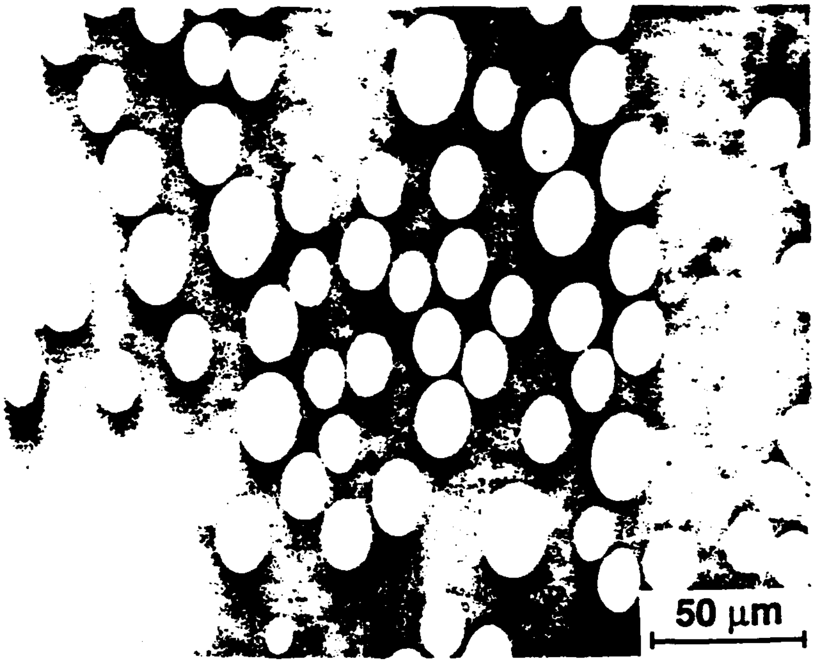
74 wt% Al_2O_3/26 wt% SiO_2
Compression $\dot{\varepsilon} = 2 \times 10^{-4}\ s^{-1}$
1300°C
1325°C
STRESS (MPa)
STRAIN
0
50
100
150
200
250
300
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7

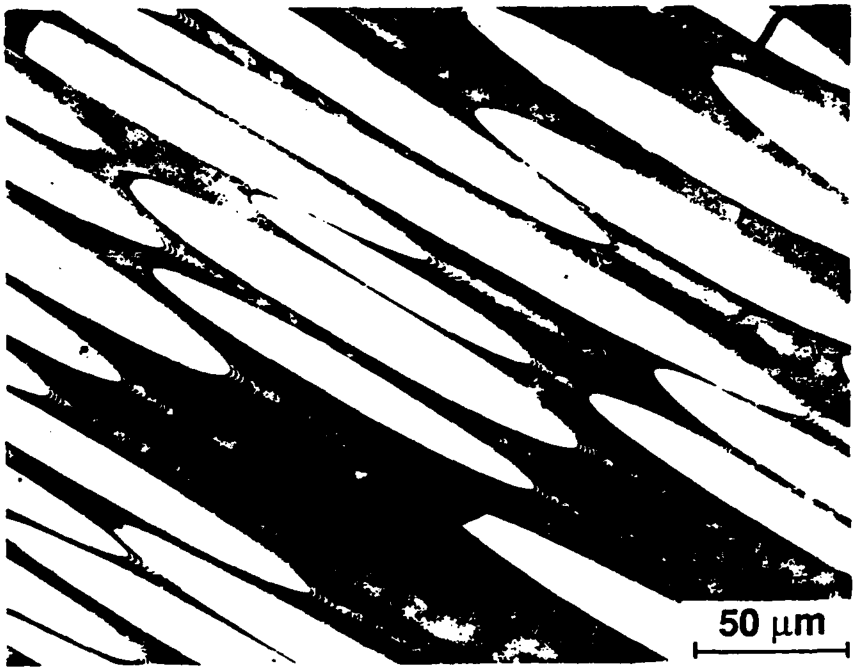

1 µm

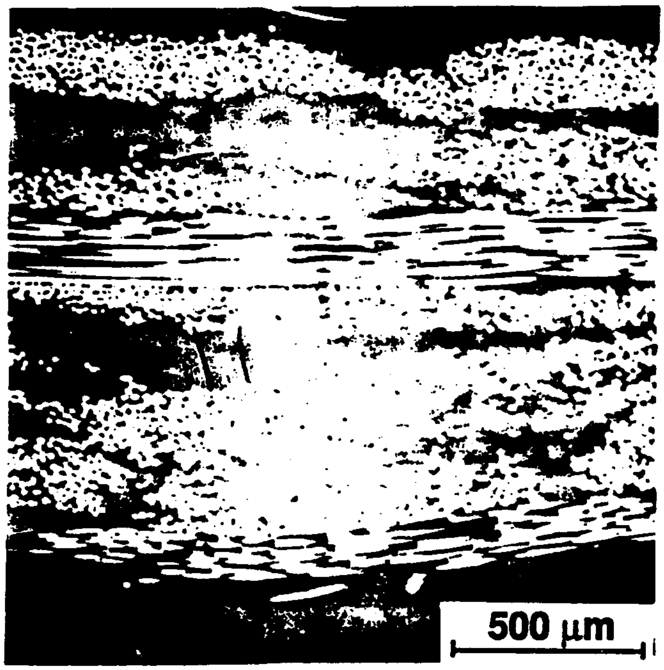

15 µm

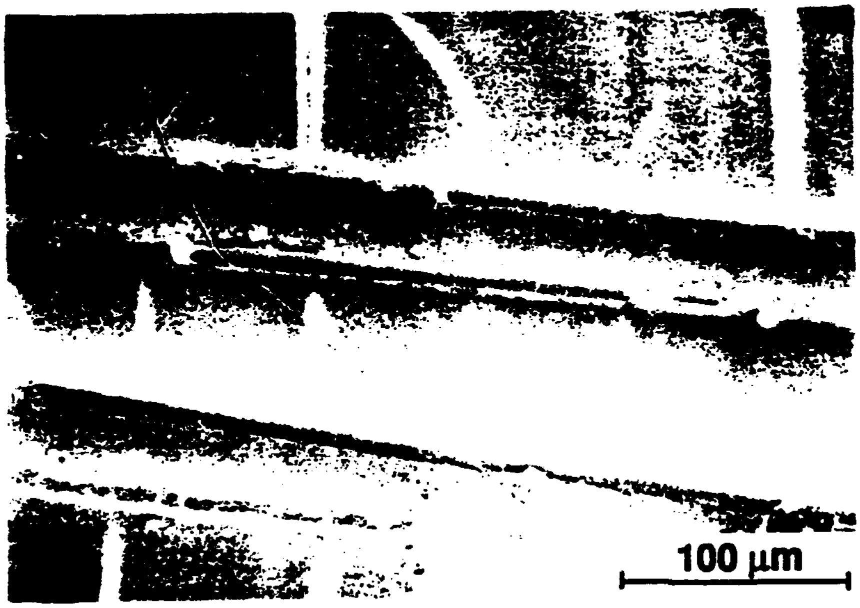

74 wt% Al_2O_3/ 26 wt% SiO_2
10 vol% SiC Fibers
1300°C Hot Press
ENGINEERING STRESS (MPa)
TIME (min)
0
10
20
30
40
50
60
70
80
0
5
10
15
20
25
30
35
40
45
50

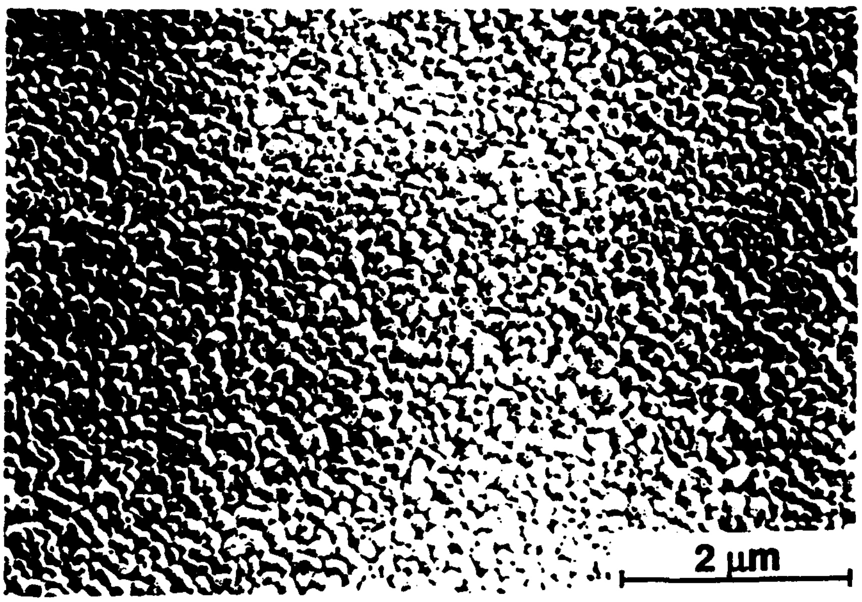

74 wt% Al_2O_3/ 26 wt% SiO_2
10 vol% SiC Fibers
1300°C Hot Press
DISPLACEMENT (mm)
TIME (min)
0
1
2
3
4
5
6
7
8
9
0
5
10
15
20
25
30
35
40
45
50


50 μm


50 μm


500 µm


100 µm


2 µm

Recent Developments in Viscous Processing

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  (fiber-reinforced composites)

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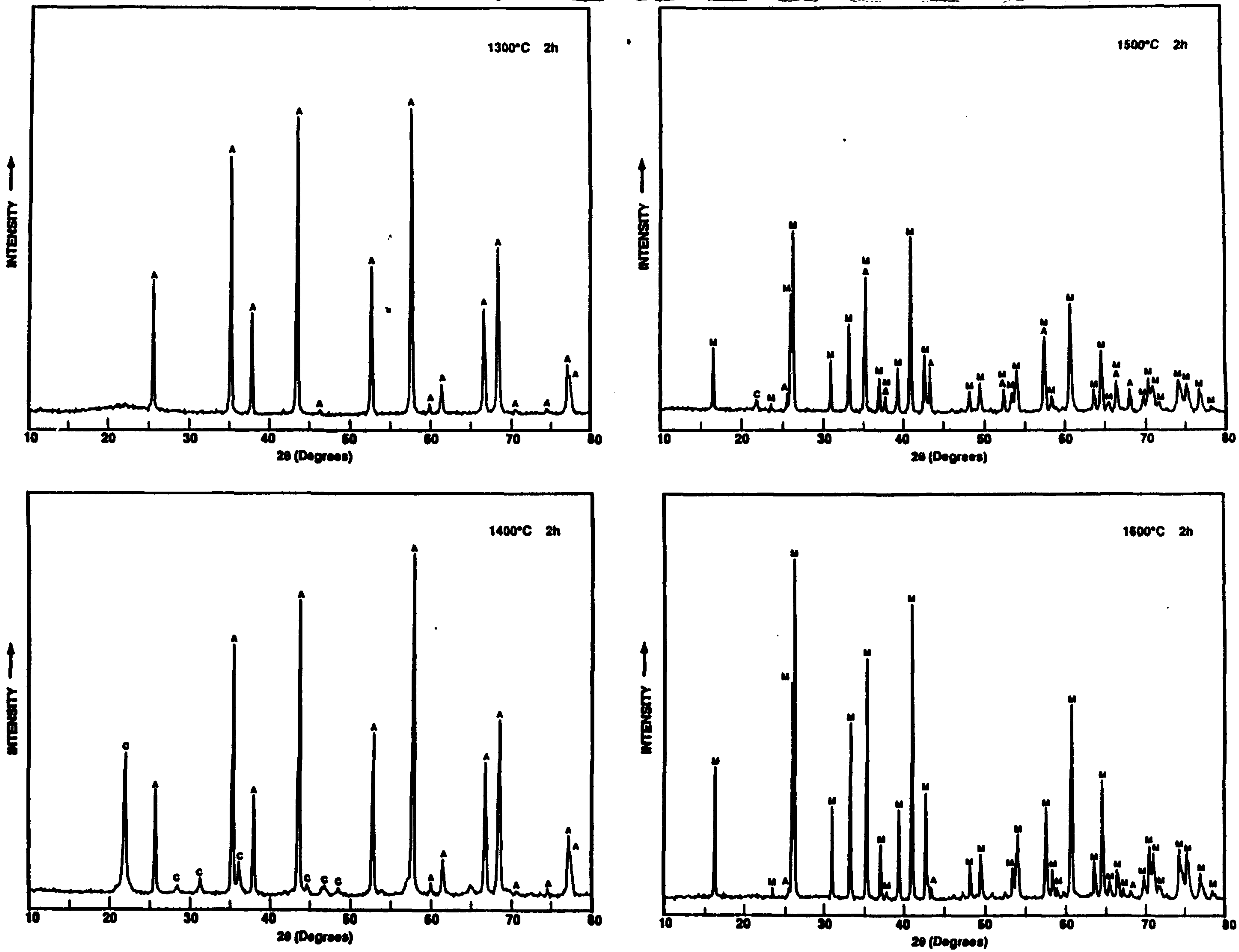
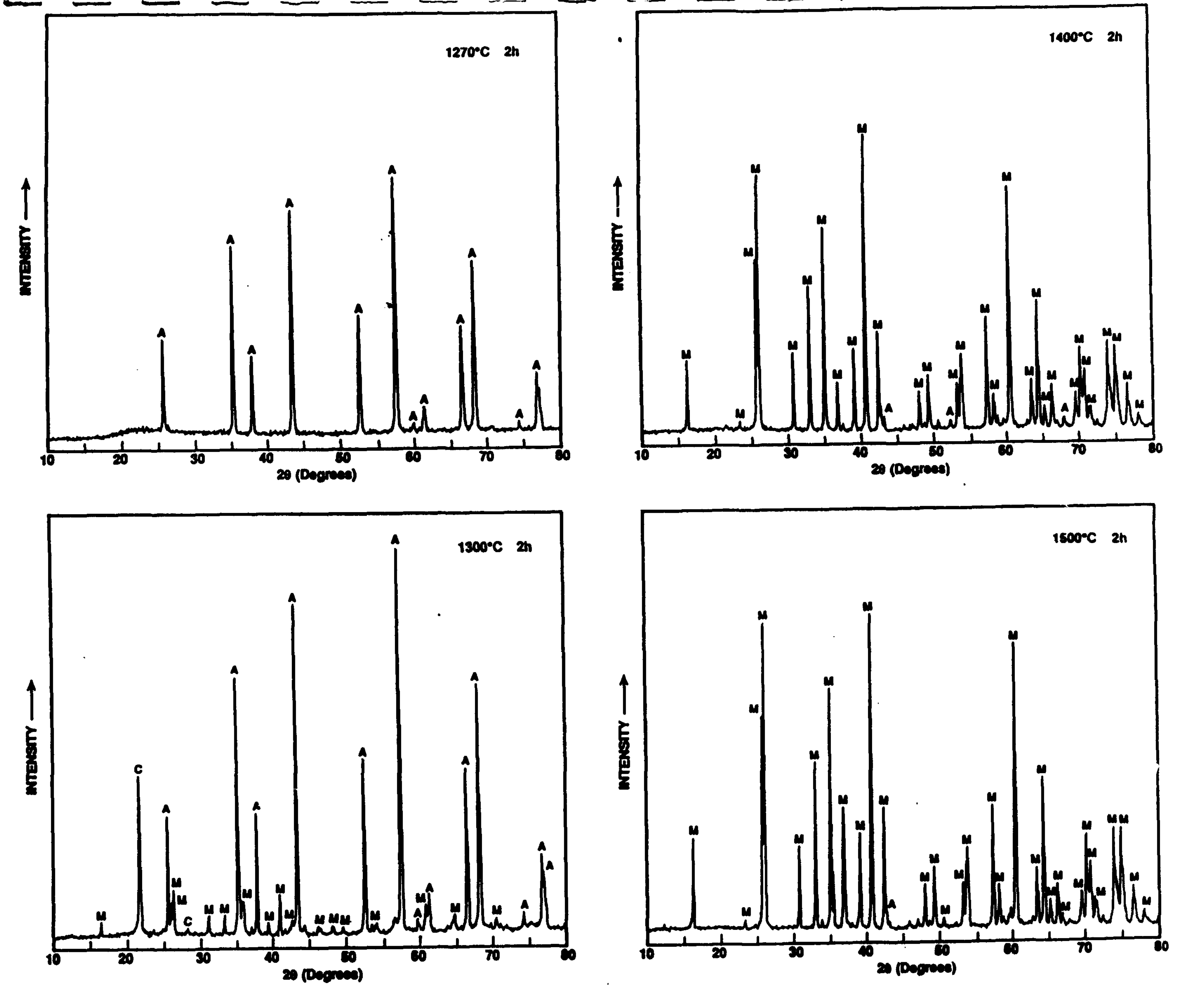
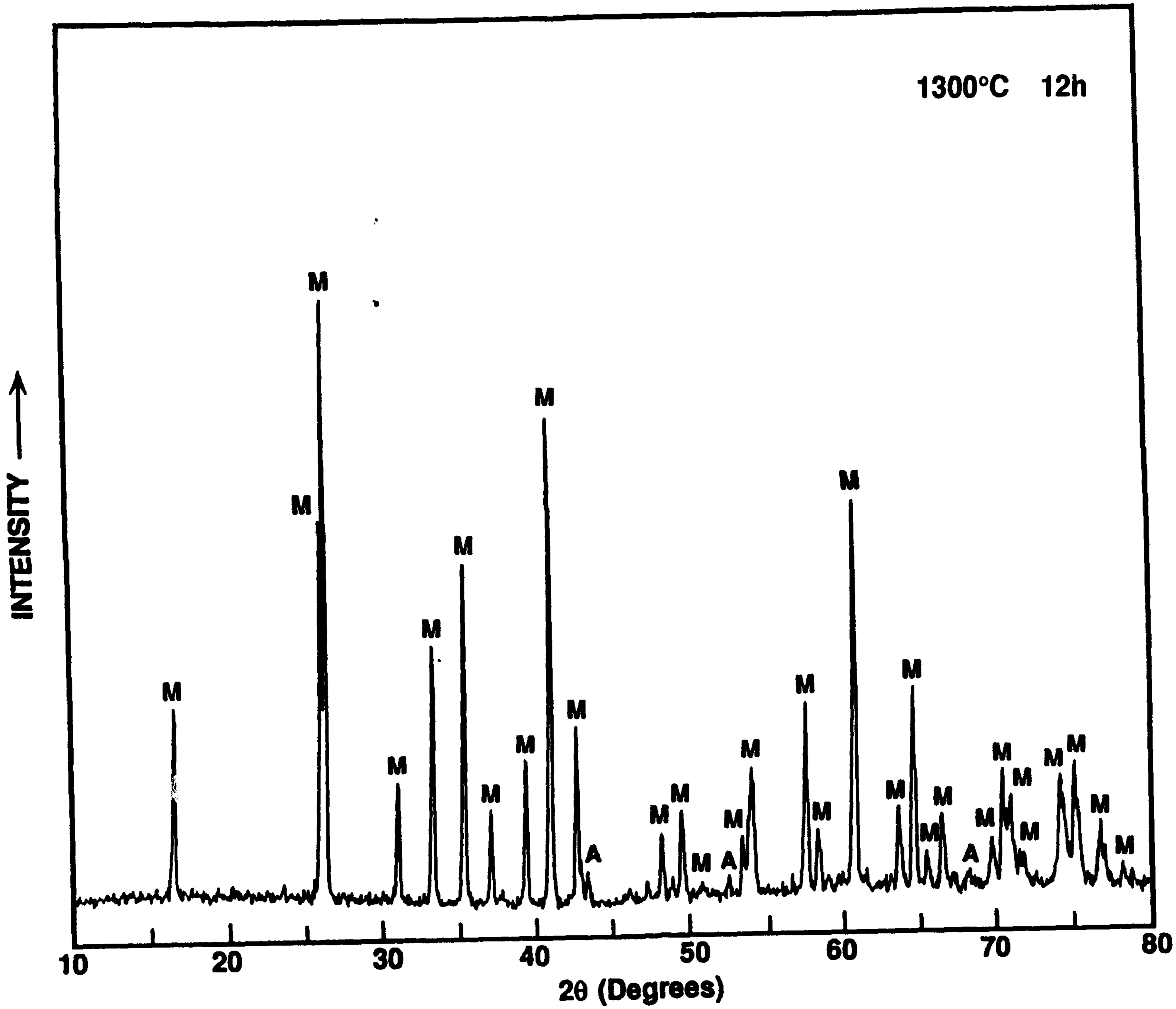
  (lower processing temperatures, finer-grain microstructures)

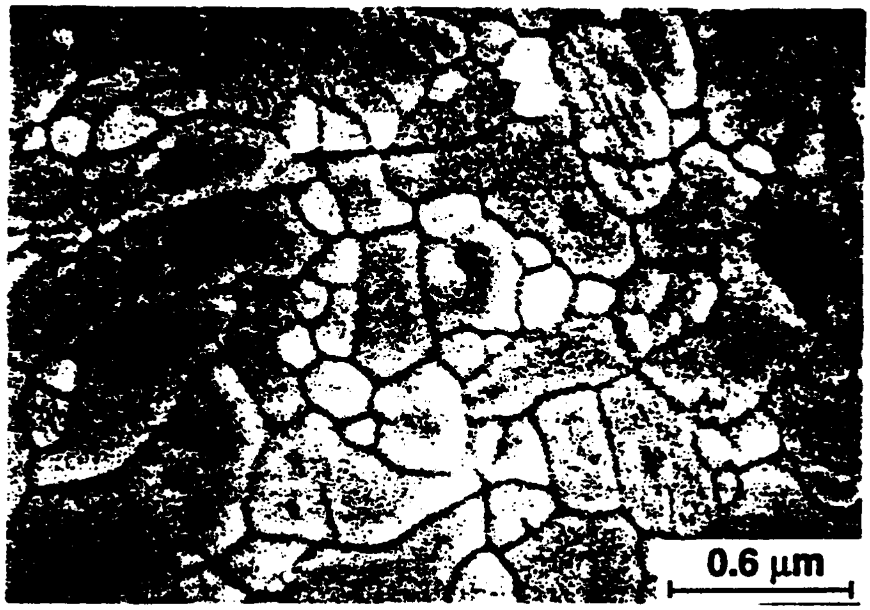
- **Microcomposite Particles with Multicomponent Coatings**
  (expanded range of compositions, lower processing temperatures)



1300°C 2h
1400°C 2h
1500°C 2h
1600°C 2h
INTENSITY
2θ (Degrees)


1270°C 2h
1300°C 2h
1400°C 2h
1500°C 2h
INTENSITY
2θ (Degrees)


1300°C 12h
INTENSITY
2θ (Degrees)
10
20
30
40
50
60
70
80
M
A


0.6 µm

Recent Developments in Viscous Processing

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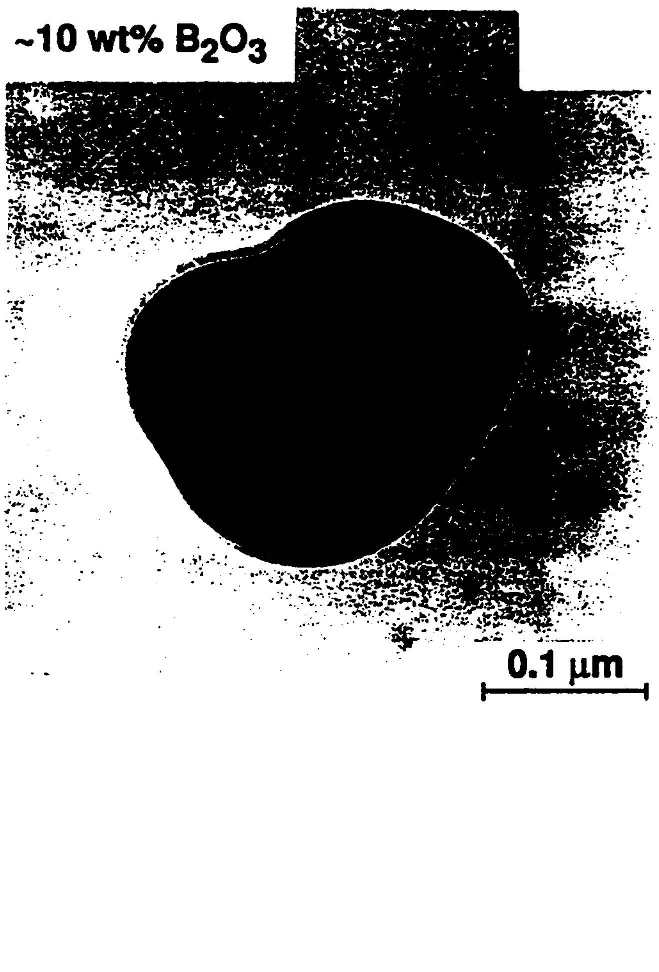
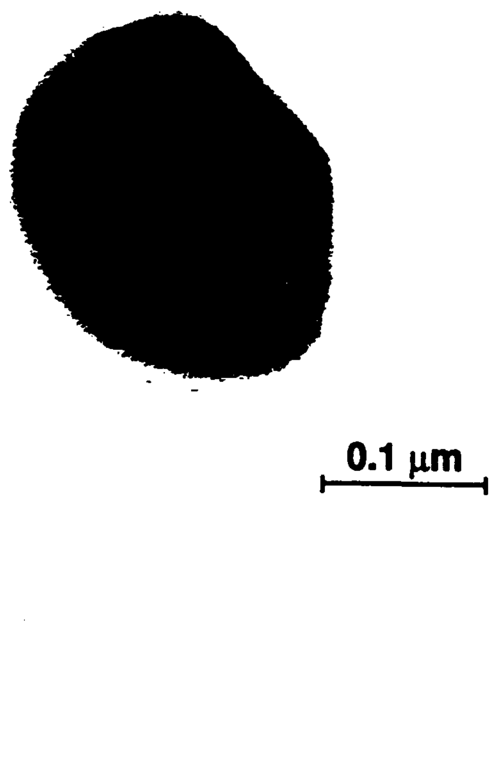
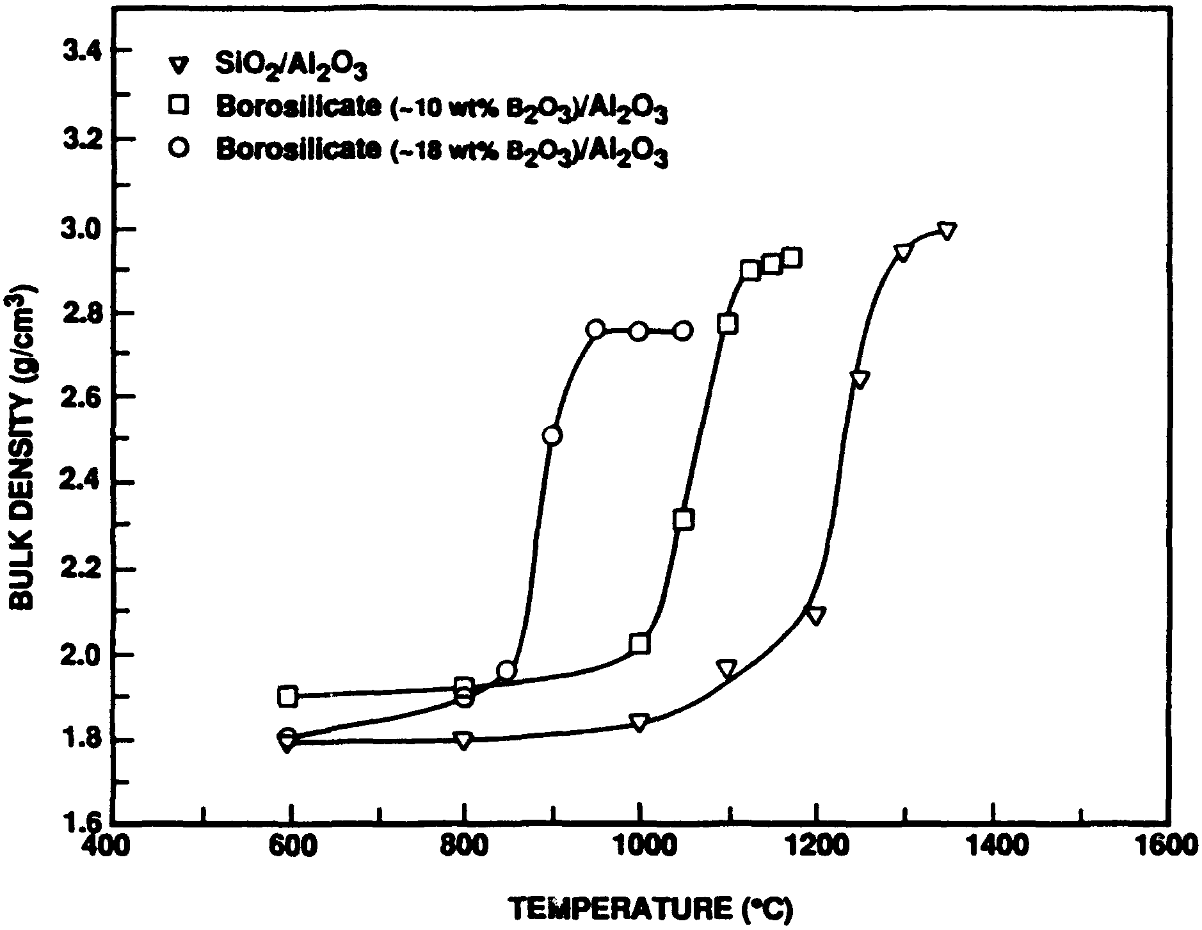
- **Microcomposite Particles with Multicomponent Coatings**
  (expanded range of compositions, lower processing temperatures)

~10 wt% B_2O_3

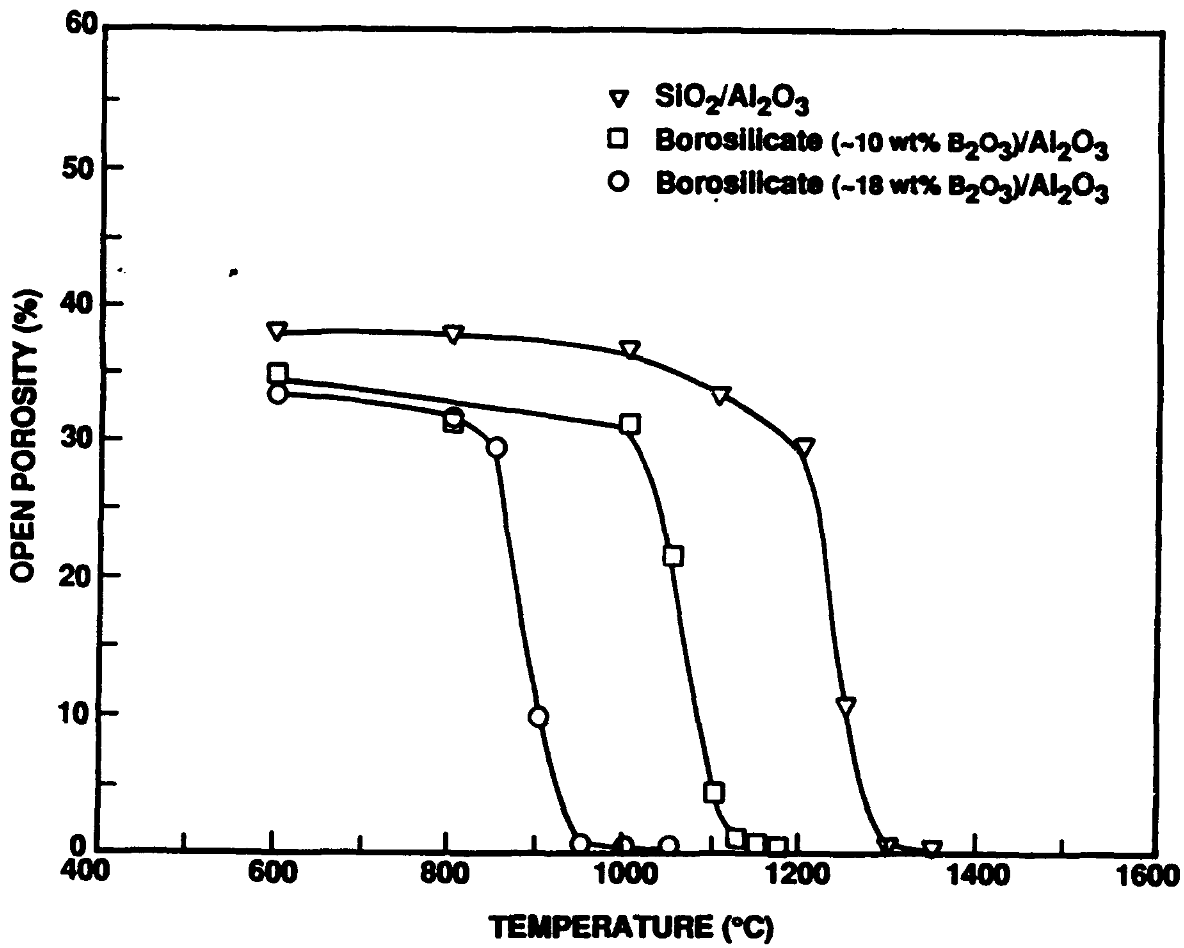


~17 wt% B_2O_3

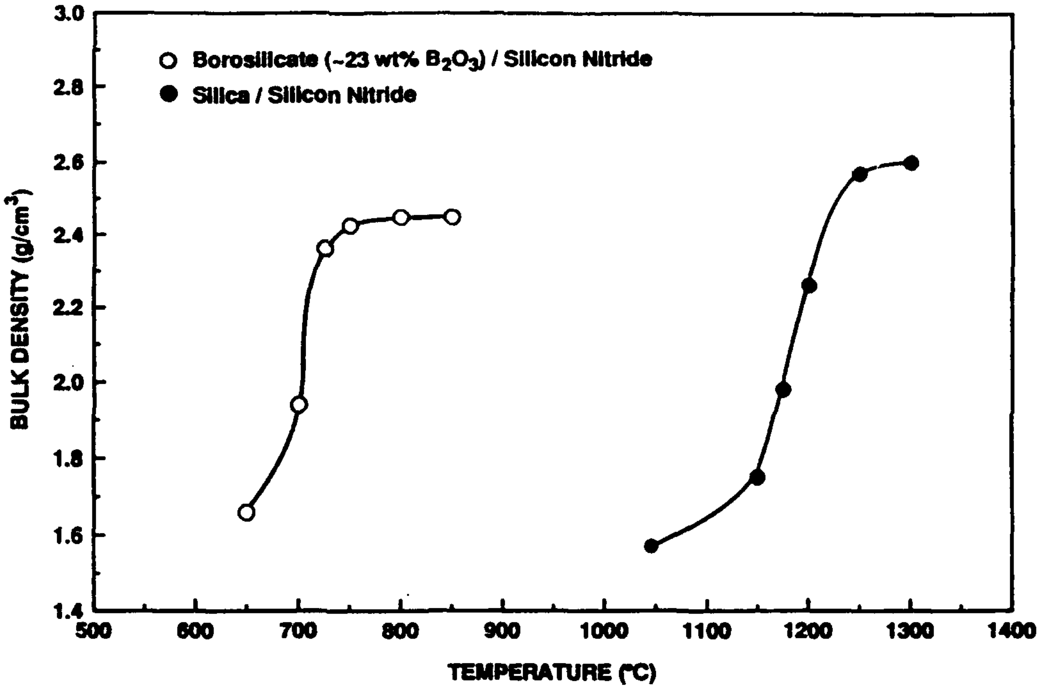


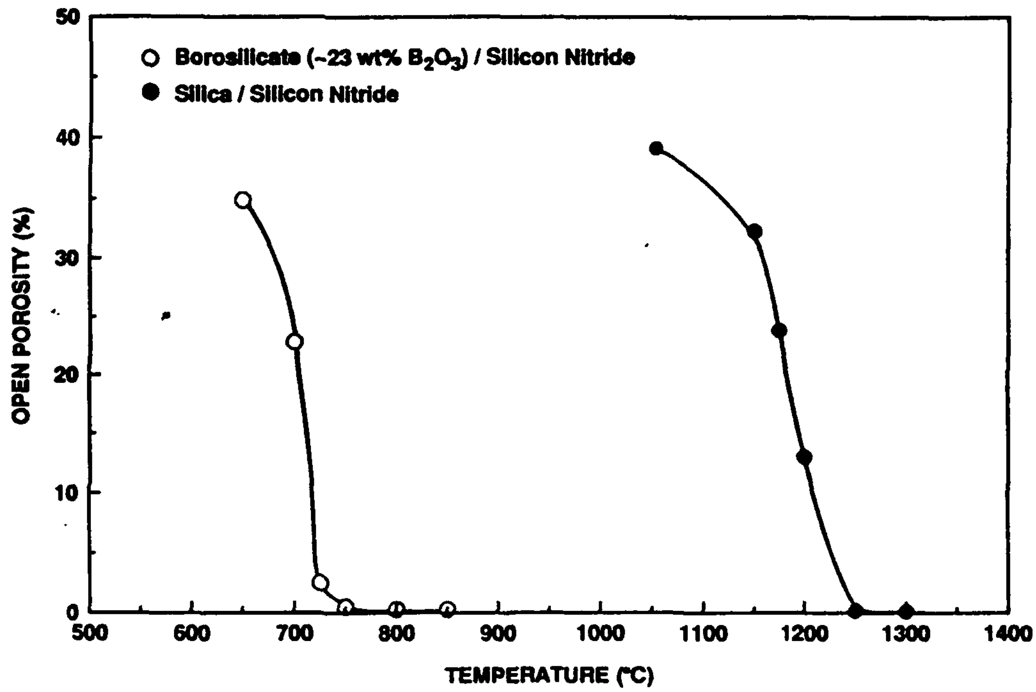


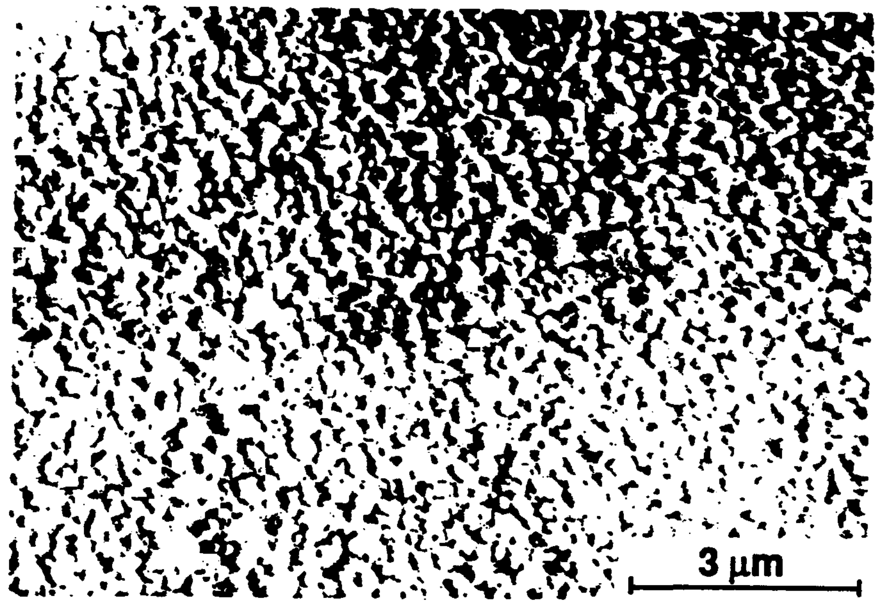
SiO2/Al2O3
Borosilicate (~10 wt% B2O3)/Al2O3
Borosilicate (~18 wt% B2O3)/Al2O3
BULK DENSITY (g/cm3)
TEMPERATURE (°C)

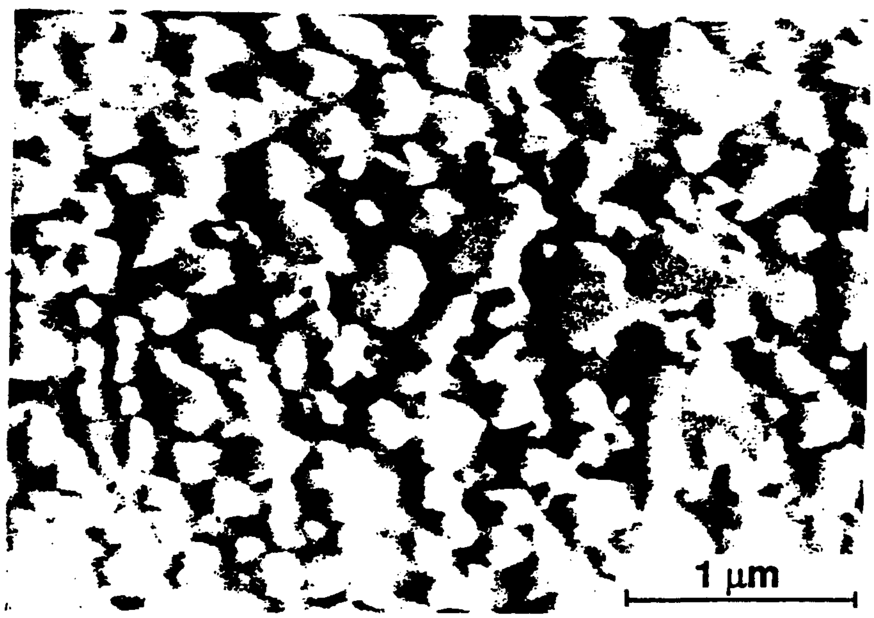


SiO2/Al2O3
Borosilicate (~10 wt% B2O3)/Al2O3
Borosilicate (~18 wt% B2O3)/Al2O3
OPEN POROSITY (%)
TEMPERATURE (°C)


Borosilicate (~23 wt% B_2O_3) / Silicon Nitride
Silica / Silicon Nitride
BULK DENSITY (g/cm^3)
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
500
600
700
800
900
1000
1100
1200
1300
1400
TEMPERATURE (°C)


Borosilicate (~23 wt% B_2O_3) / Silicon Nitride
Silica / Silicon Nitride
OPEN POROSITY (%)
50
40
30
20
10
0
500
600
700
800
900
1000
1100
1200
1300
1400
TEMPERATURE (°C)


3 μm


1 μm

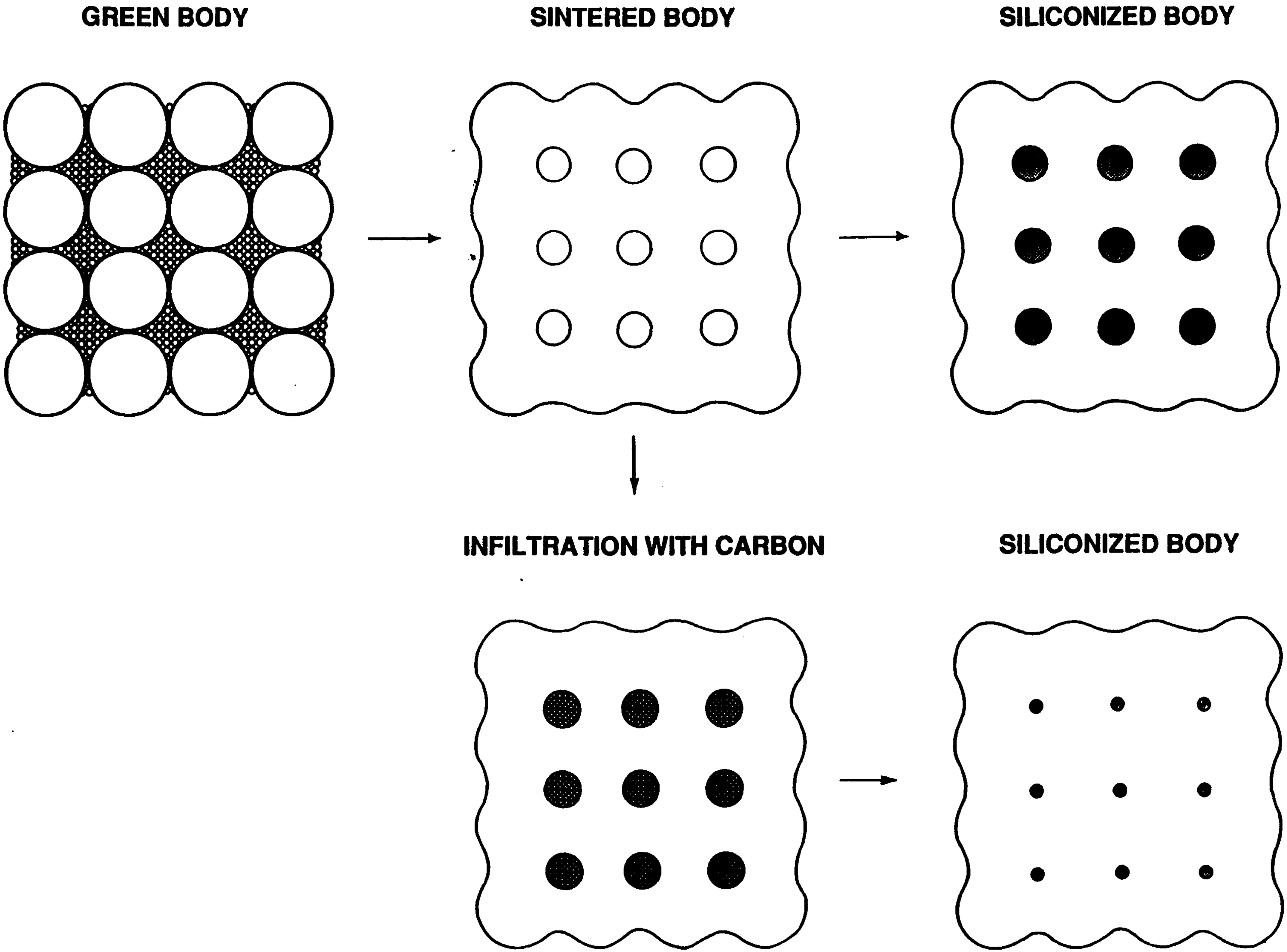
Reactive Infiltration of Metals (RIM)

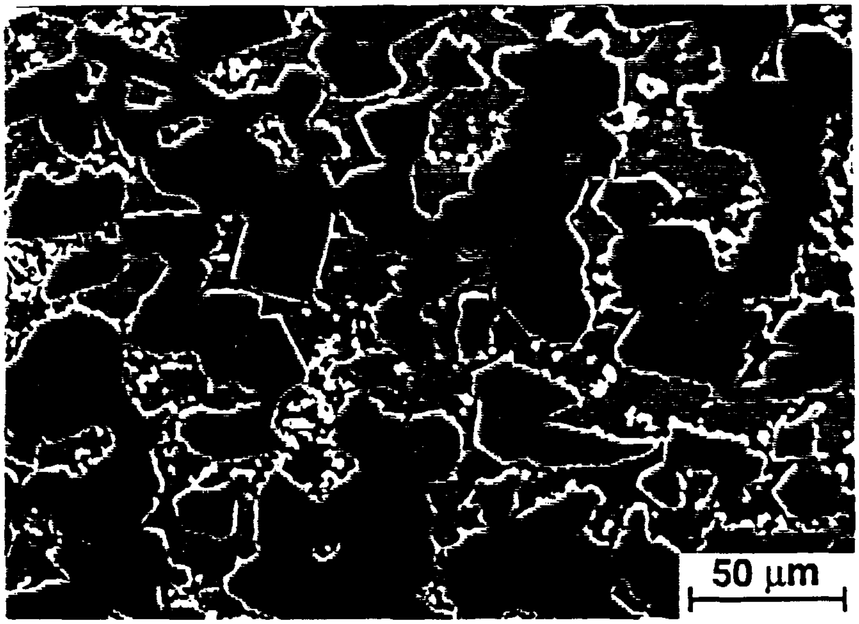
Objectives

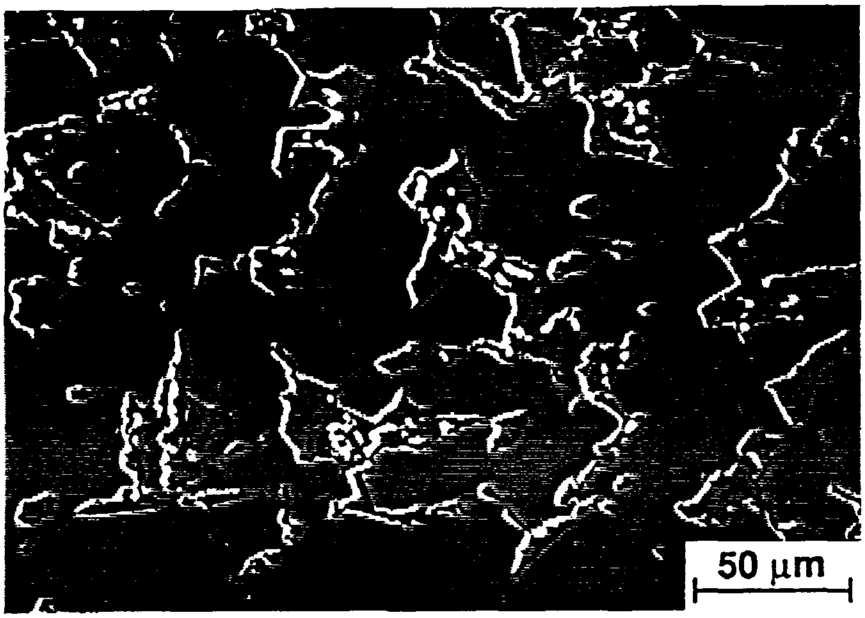
- Densification with little or no shrinkage
- SiC-based composites with little or no residual metal

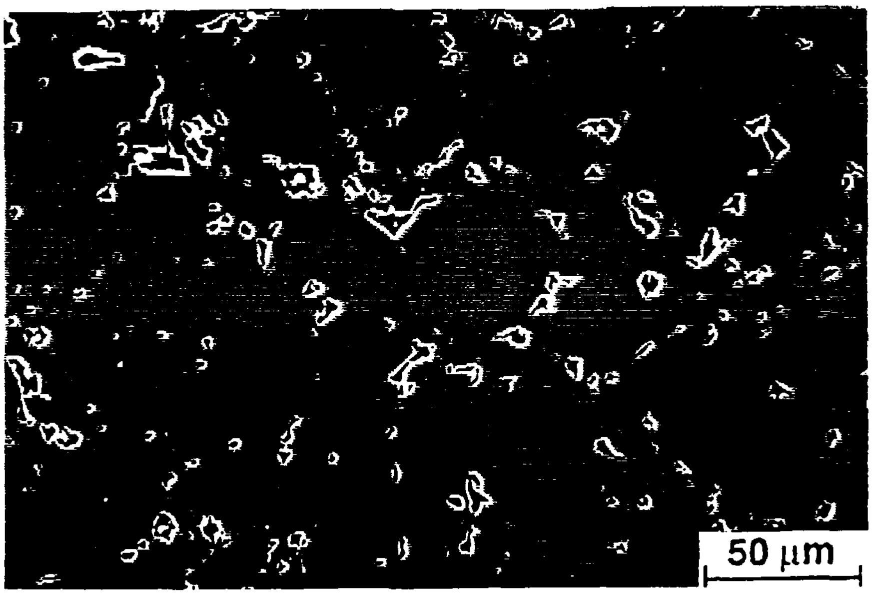
Approach

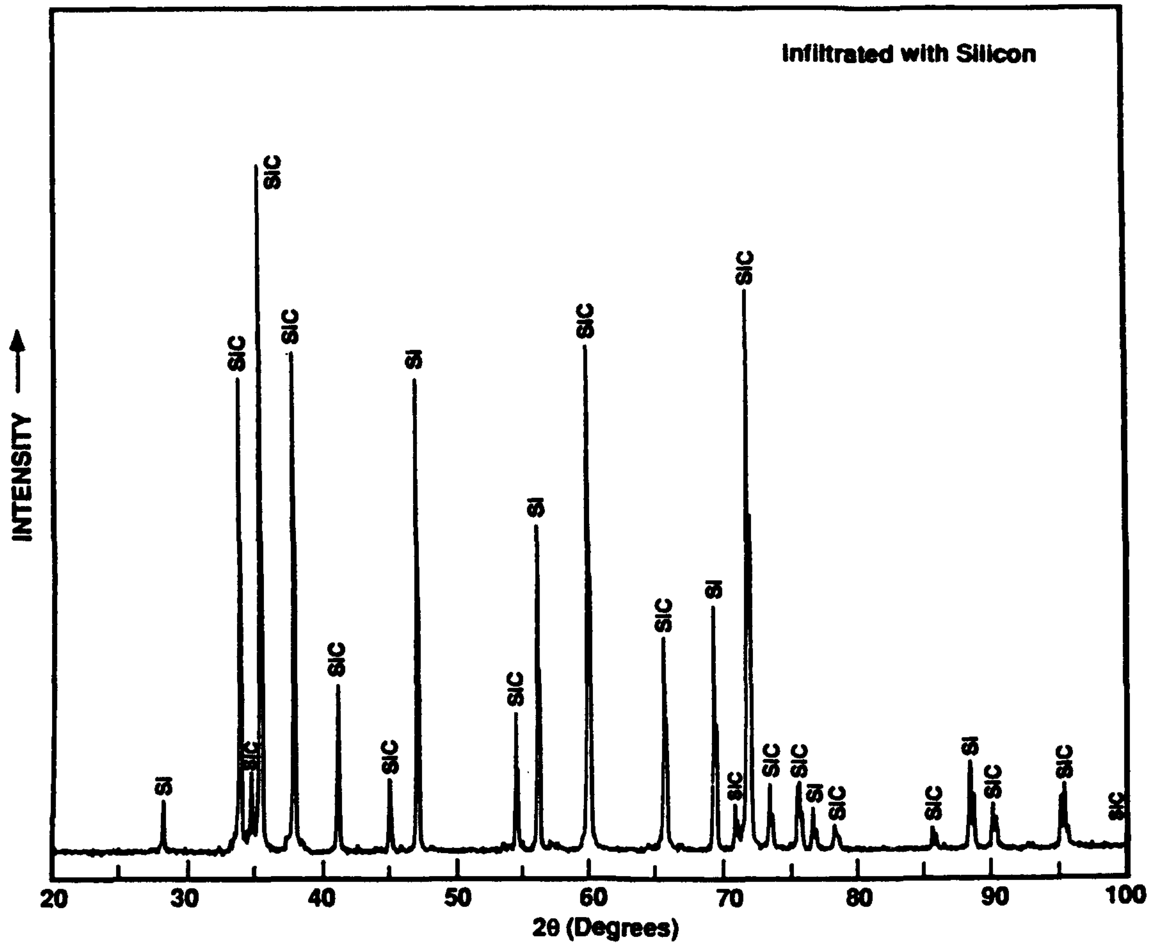
- Low temperature infiltration of carbon precursor and high temperature infiltration of silicon alloy.

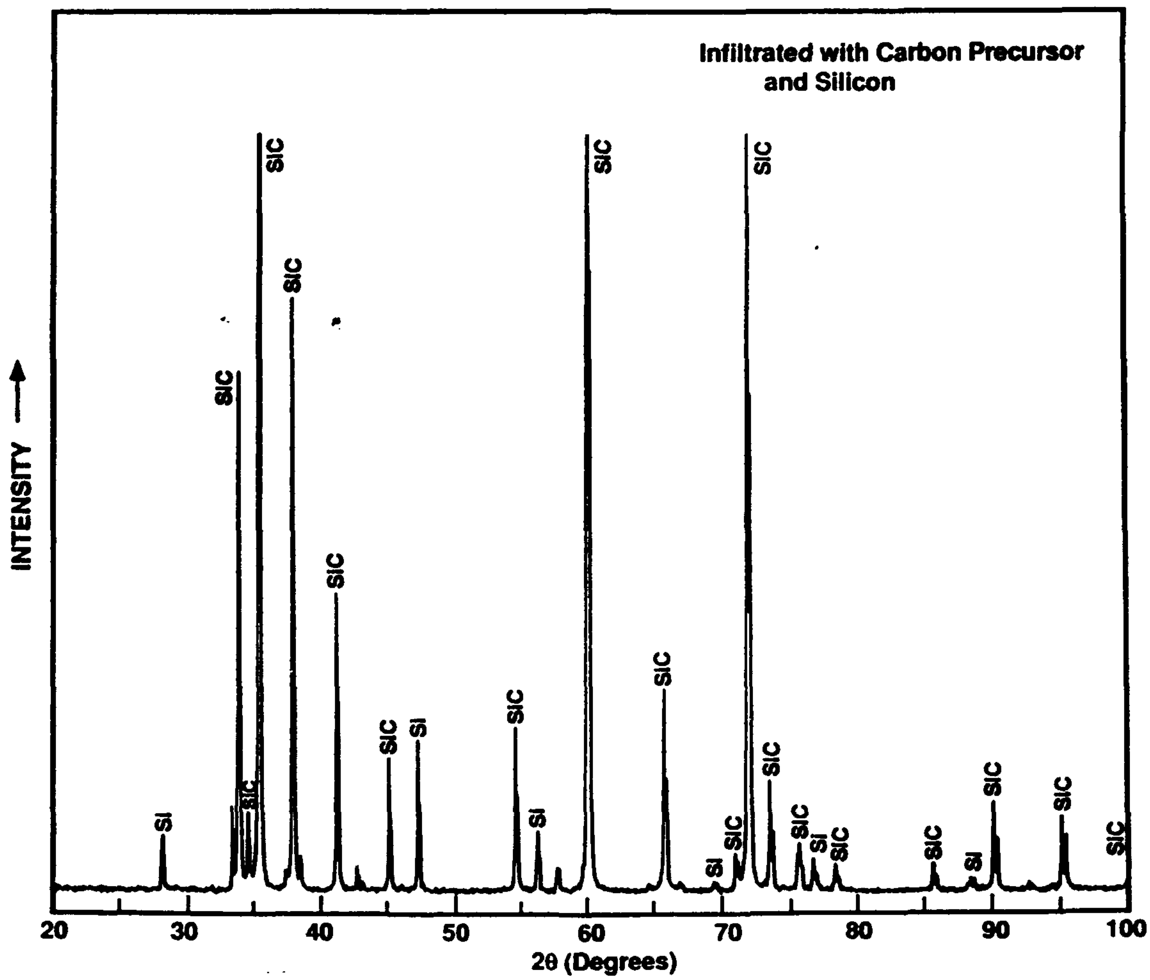

GREEN BODY
SINTERED BODY
SILICONIZED BODY
INFILTRATION WITH CARBON
SILICONIZED BODY

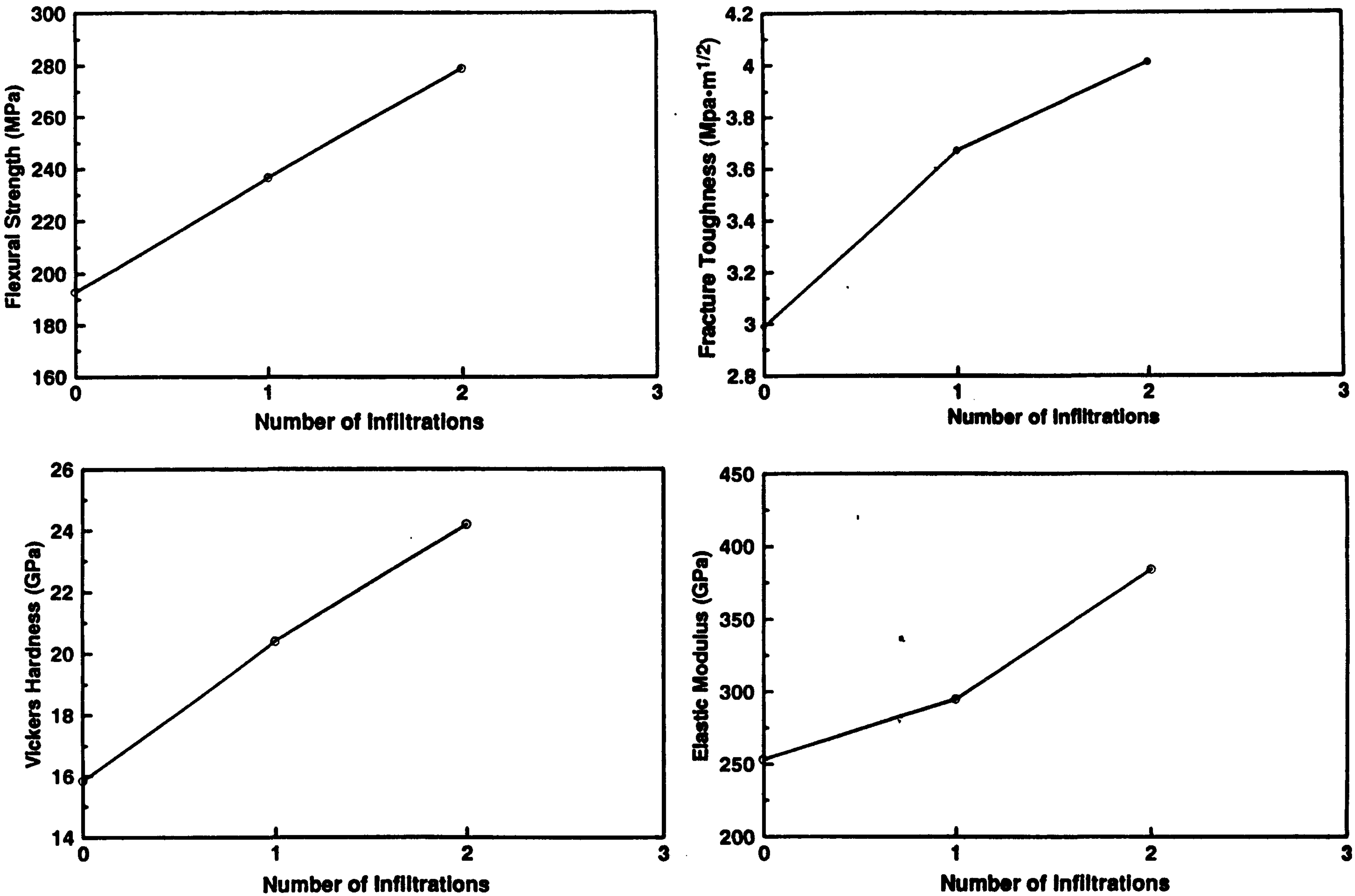

50 µm

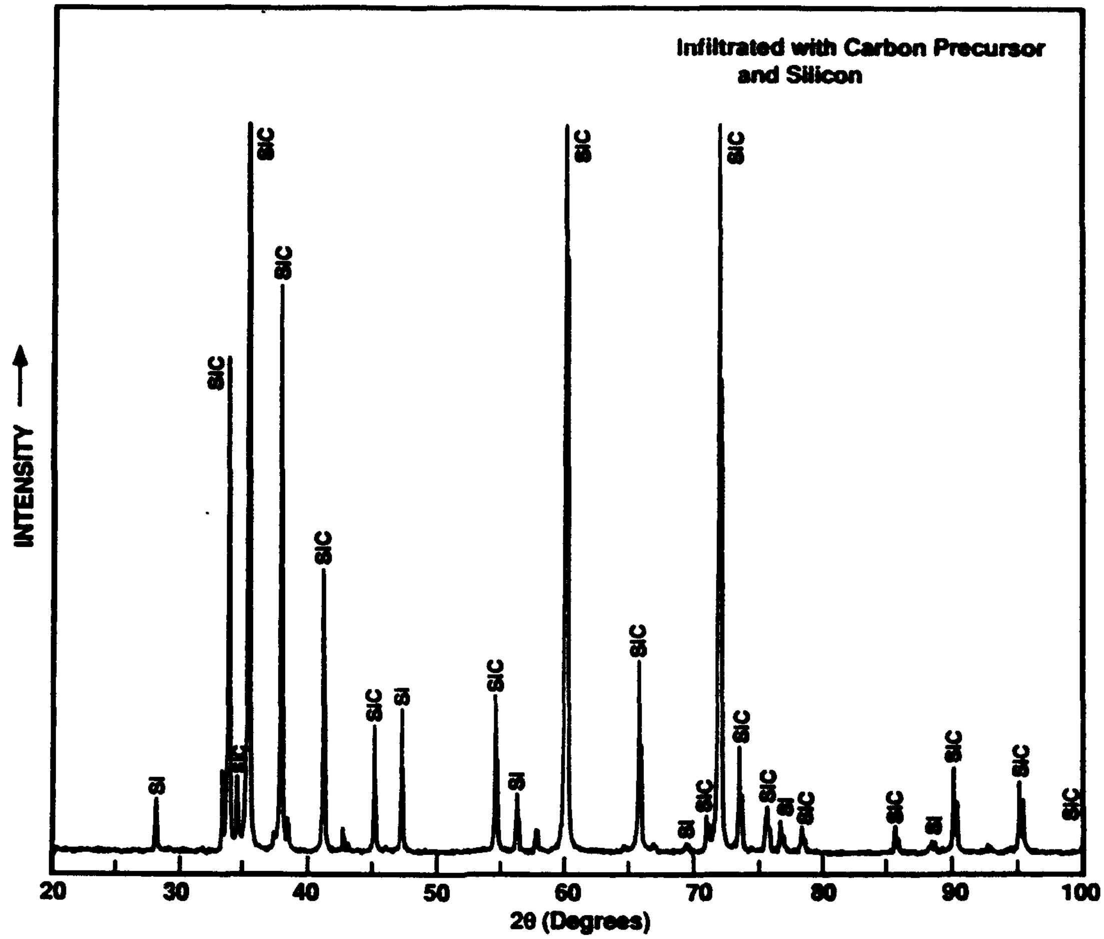

50 µm

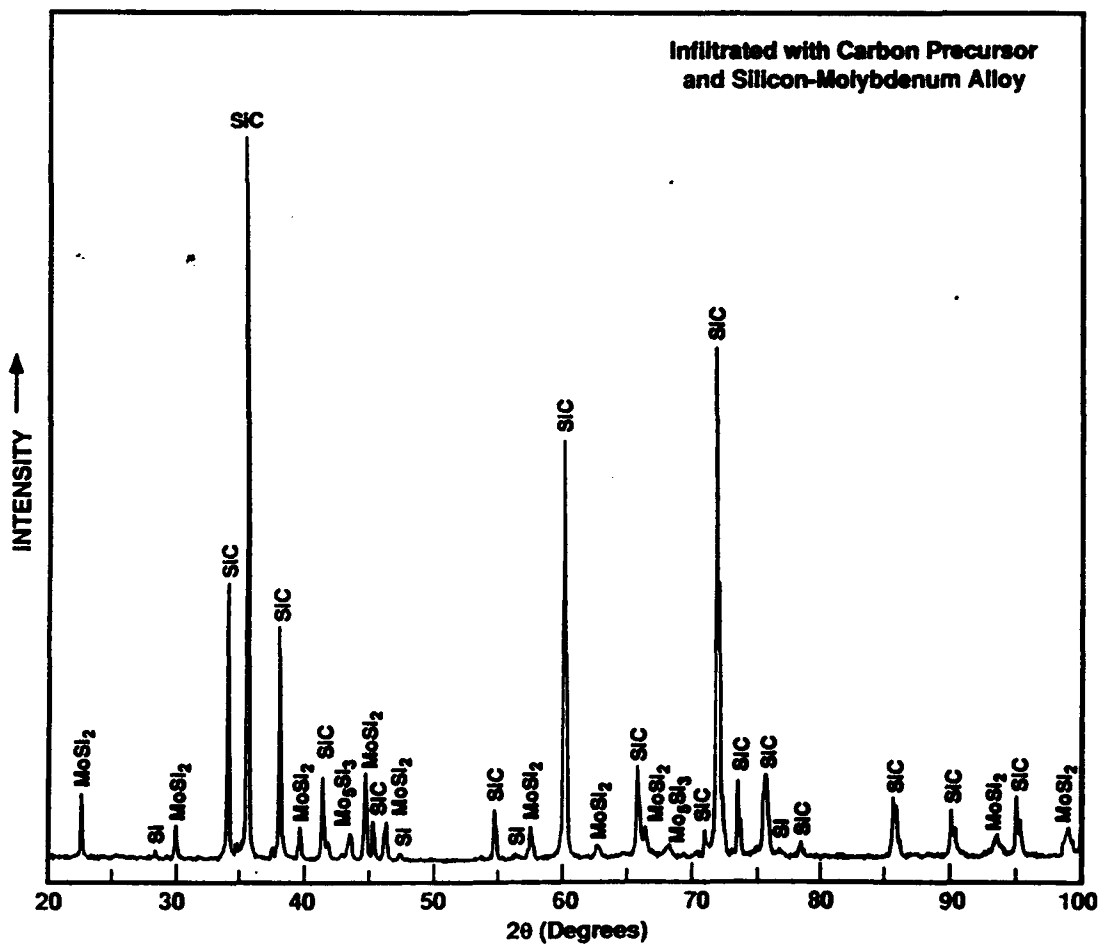

50 µm

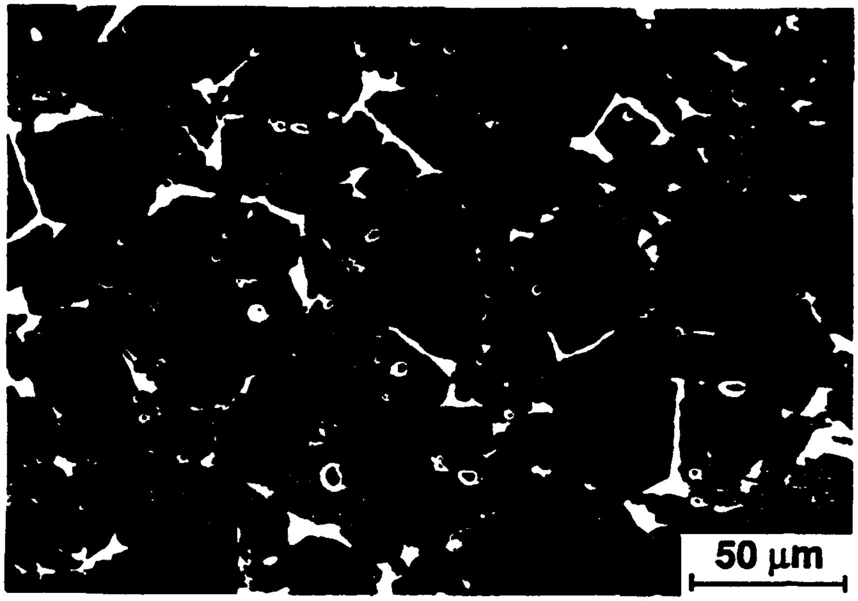

Infiltrated with Silicon
INTENSITY
2θ (Degrees)
SI
SIC
SIC
SIC
SIC
SIC
SIC
SI
SIC
SI
SIC
SIC
SI
SIC
SIC
SIC
SIC
SI
SIC
SIC
SI
SIC
SIC
SIC
20
30
40
50
60
70
80
90
100


Infiltrated with Carbon Precursor
and Silicon
INTENSITY
2θ (Degrees)
SI
SIC
SIC
SIC
SIC
SIC
SIC
SI
SIC
SI
SIC
SIC
SI
SIC
SIC
SIC
SIC
SI
SIC
SIC
SI
SIC
SIC
SIC
20
30
40
50
60
70
80
90
100

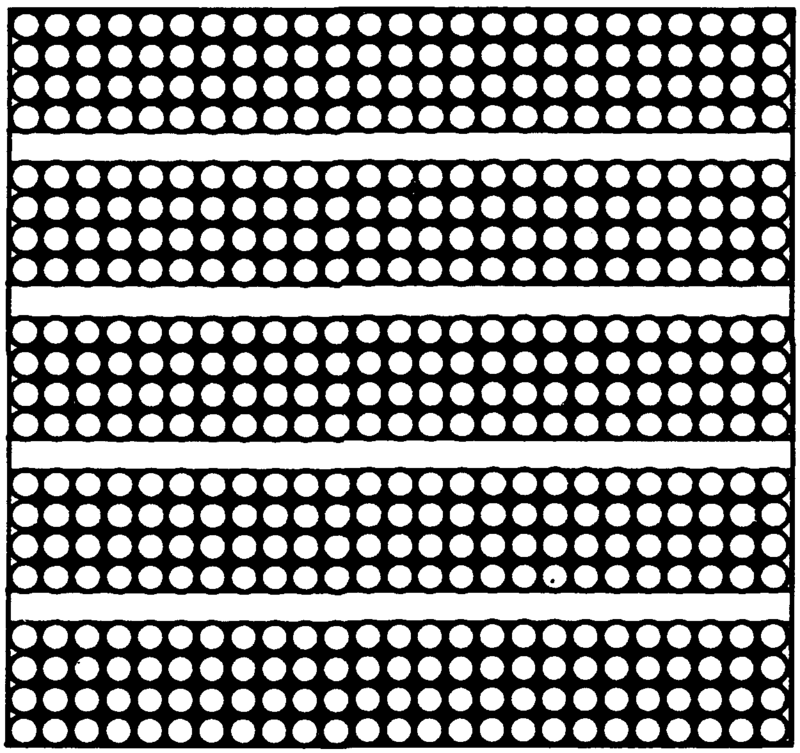

Flexural Strength (MPa)
300
280
260
240
220
200
180
160
0
1
2
3
Number of Infiltrations
Fracture Toughness (Mpa·m1/2)
4.2
4
3.8
3.6
3.4
3.2
3
2.8
Vickers Hardness (GPa)
26
24
22
20
18
16
14
Elastic Modulus (GPa)
450
400
350
300
250
200

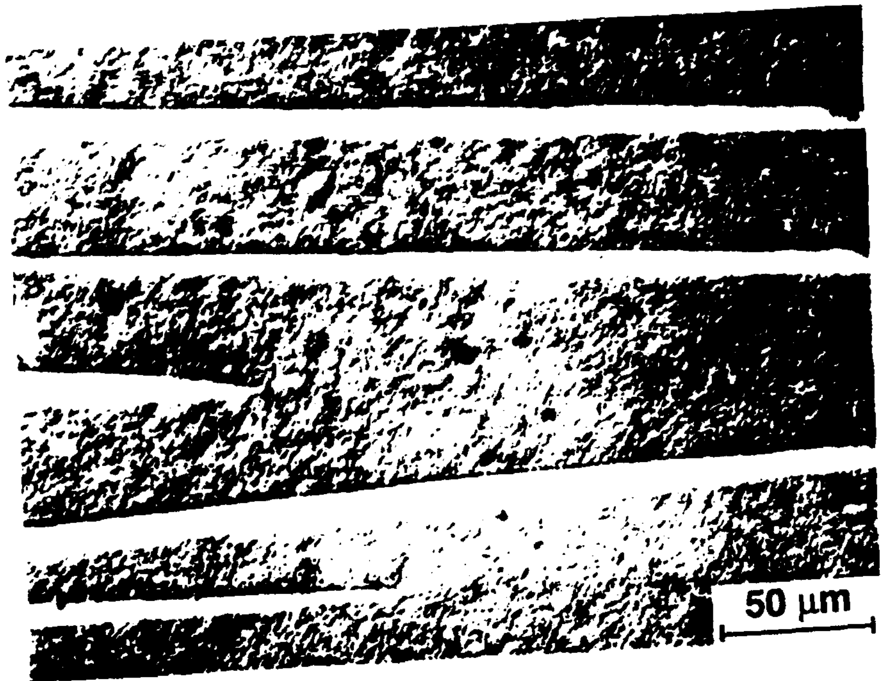

Infiltrated with Carbon Precursor
and Silicon
INTENSITY
SiC
Si
20
30
40
50
60
70
80
90
100
2θ (Degrees)

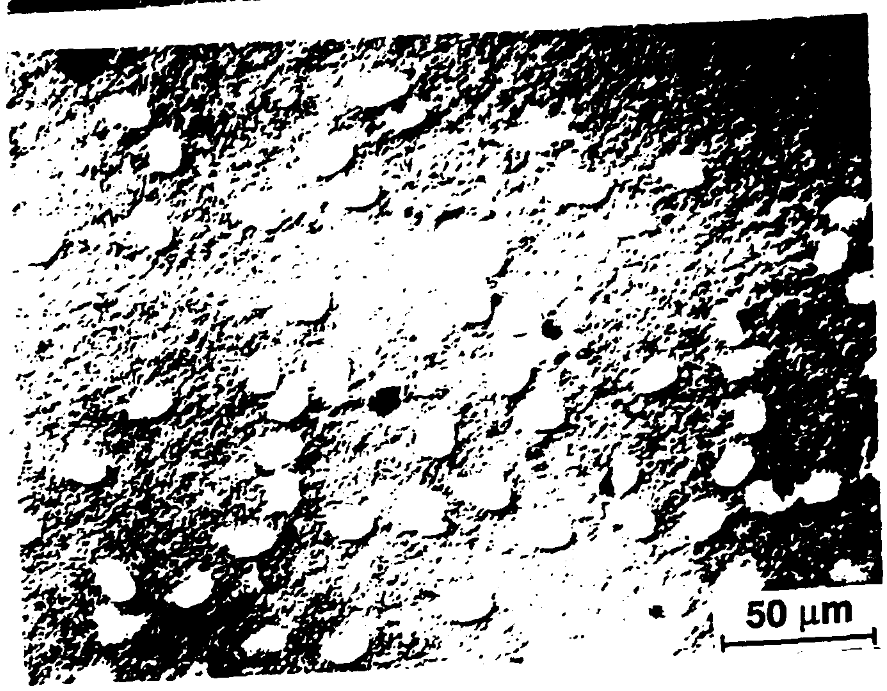

Infiltrated with Carbon Precursor
and Silicon-Molybdenum Alloy
INTENSITY
SiC
Si
MoSi2
Mo5Si3
20
30
40
50
60
70
80
90
100
2θ (Degrees)


50 µm

Fiber-Reinforced Green Body




50 µm


50 µm

SUMMARY

Viscous Processing of Microcomposite Particles

- Fabrication of a Wide Range of Ceramics, Glass/Ceramic Composites, and Ceramic/Ceramic Composites
- Low Temperature Densification by Viscous Flow
- Unique Microstructures (e.g., High Volume Fraction of Well-Dispersed Inclusions)
- Hot Forming of Shapes

Reactive Infiltration of Metals

- SiC-Based Composites with Low Residual Si Content
- High Density (Low Porosity) Achieved without Shrinkage

Co-Workers

G.W. Scheiffele
N. Bozkurt
I.Y. Park
R.Raghunathan
K. Wang
Y.J. Lin
A.E. Bagwell
A.J. Ulicny

TAPECAST LAMINATED COMPOSITES

ZHENG CHEN & J. J. MECHOLSKY, JR.

DEPARTMENT OF MATERIALS SCIENCE & ENGINEERING

UNIVERSITY OF FLORIDA

OBJECTIVES:

- DEVELOP A DESIGN METHODOLOGY FOR TAILORED COMPOSITE STRUCTURES TO INHIBIT CRACK INITIATION AND PROPAGATION
- MEASURE PROPERTIES OF CERAMIC MATRIX - METALLIC LAMINATED COMPOSITES

DARPA

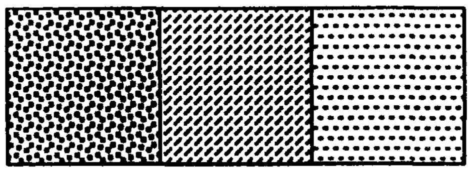
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

PROGRESS

- PRODUCED LAMINATES WHOSE STRENGTHS ARE CRACK SIZE INDEPENDENT.
- DEVELOPED A DESIGN METHODOLOGY TO CONTROL LAMINAE INTERFACES.
- IMPROVED LAMINATE TOUGHNESS TO >10MPam$^{1/2}$ USING FUNCTIONALLY GRADED DESIGN.
- IMPROVED THERMAL SHOCK RESISTANCE OF ALUMINA UP TO $\Delta T = 1200°C$.
- ACHIEVED LAMINATE STRENGTHS > 700 MPa.

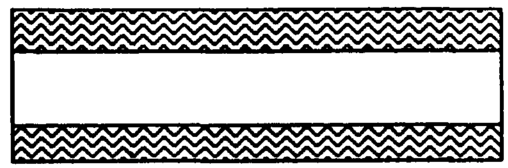
Toughening Can Occur Using Different Mechanisms

SECOND PHASE



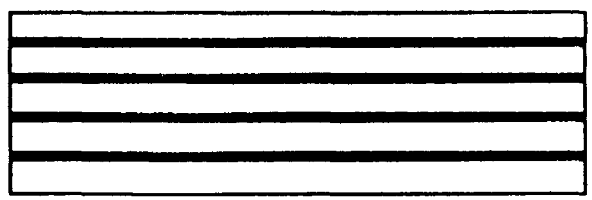
COMPOSITES
(e.g. Heitzenrater)

RESIDUAL COMPRESSION



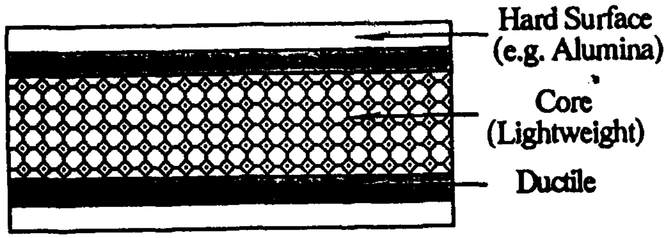
HYBRID LAMINATES
(Amateau and Messing)

DUCTILE LAYER BRIDGING

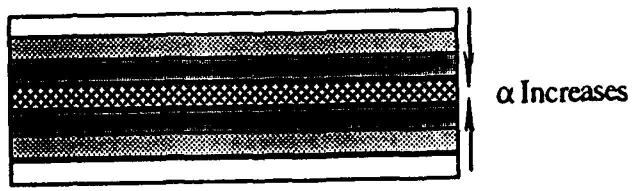


METAL-CERAMIC LAMINATES
(Evans and Cao et al.)

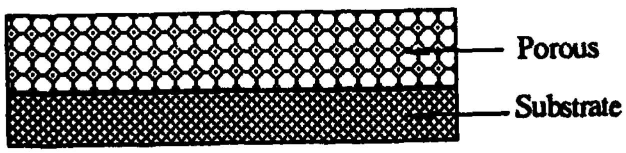
LAMINATE DESIGN OFFERS MANY POTENTIAL MULTILAYER STRUCTURES



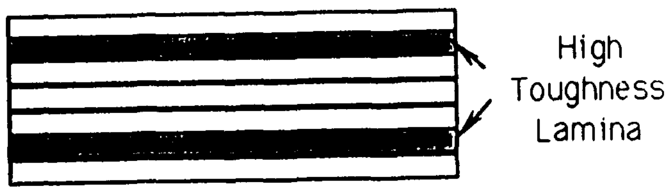
High Specific Strength



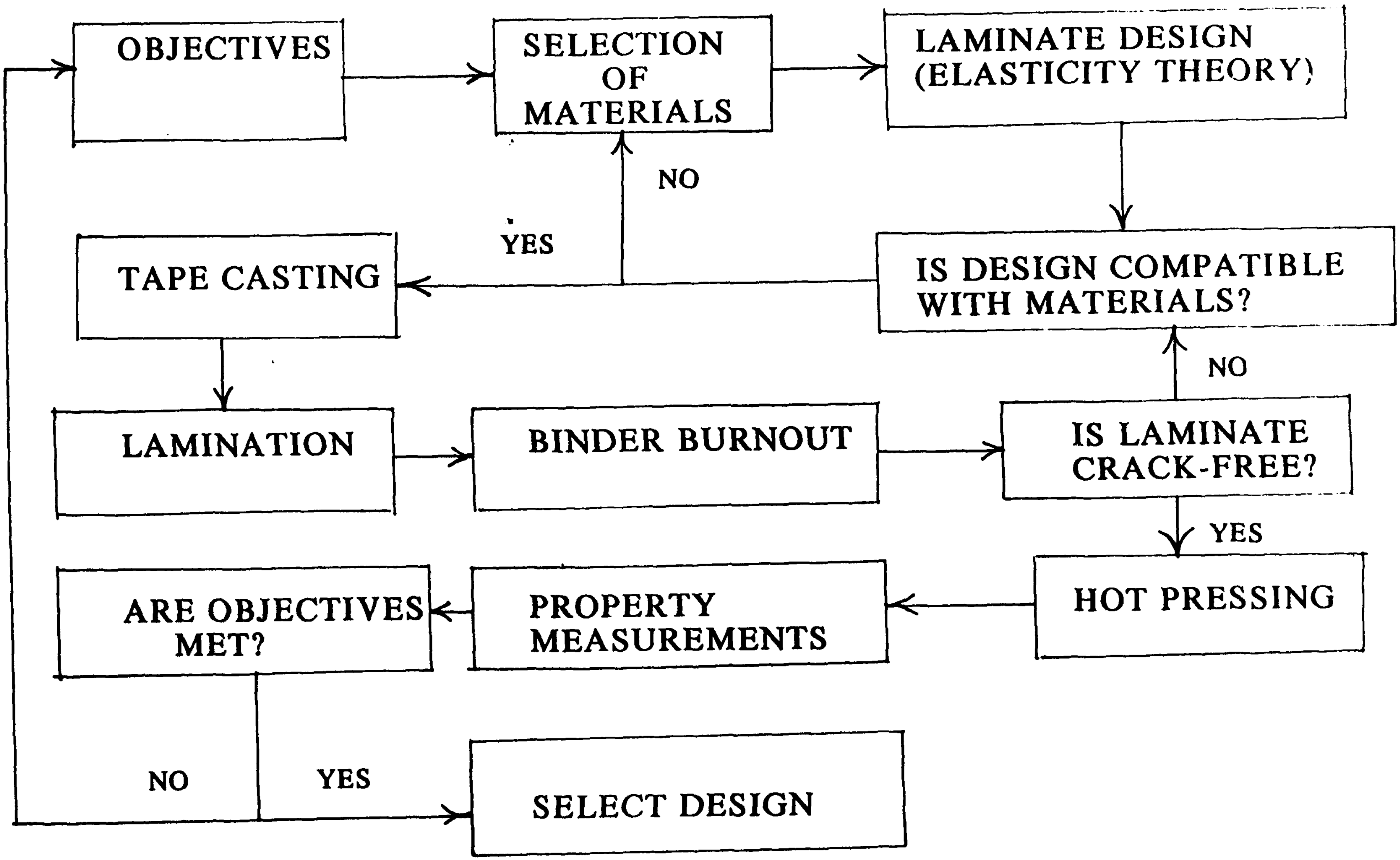
Compressive Residual Stress

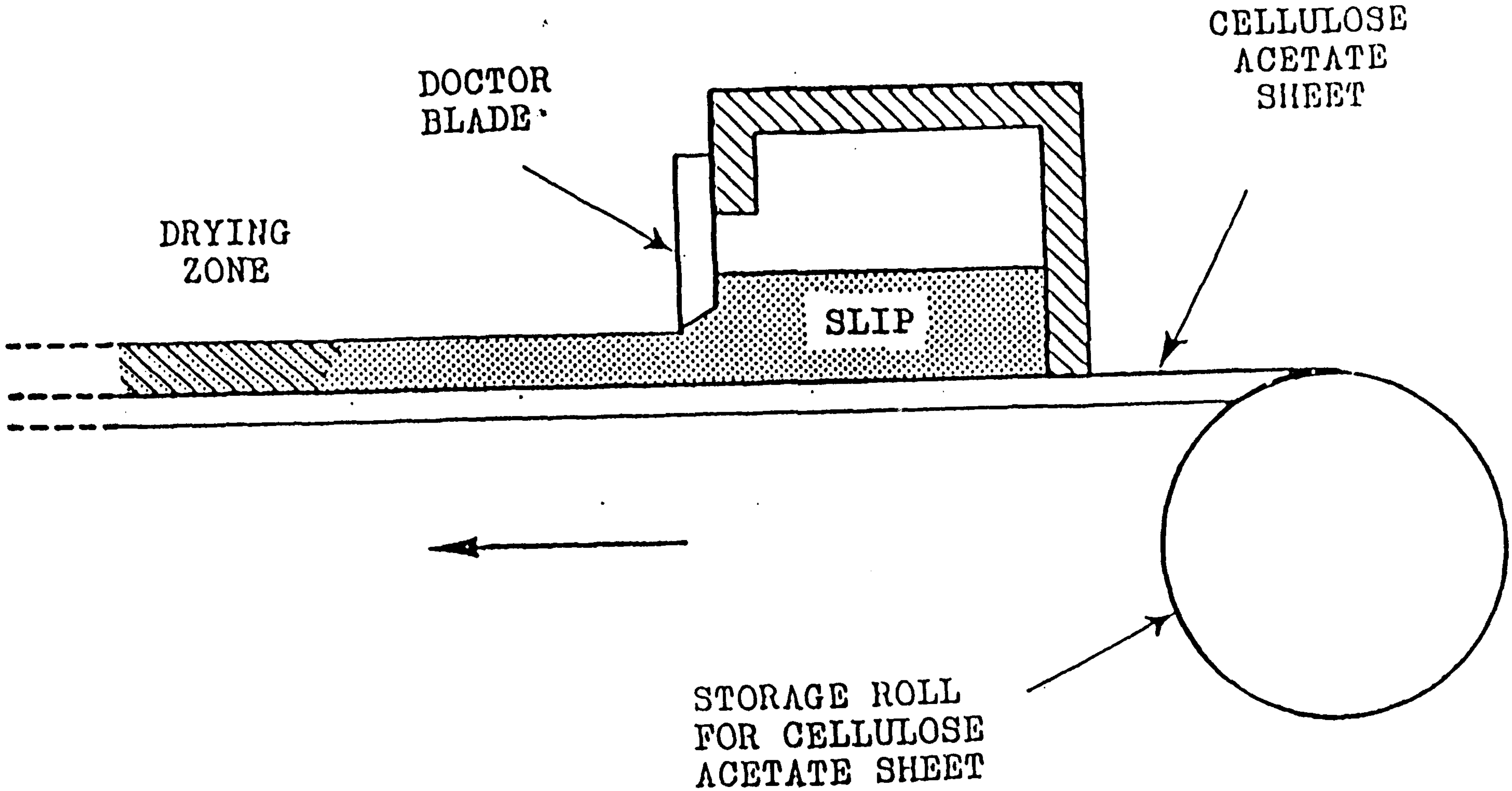


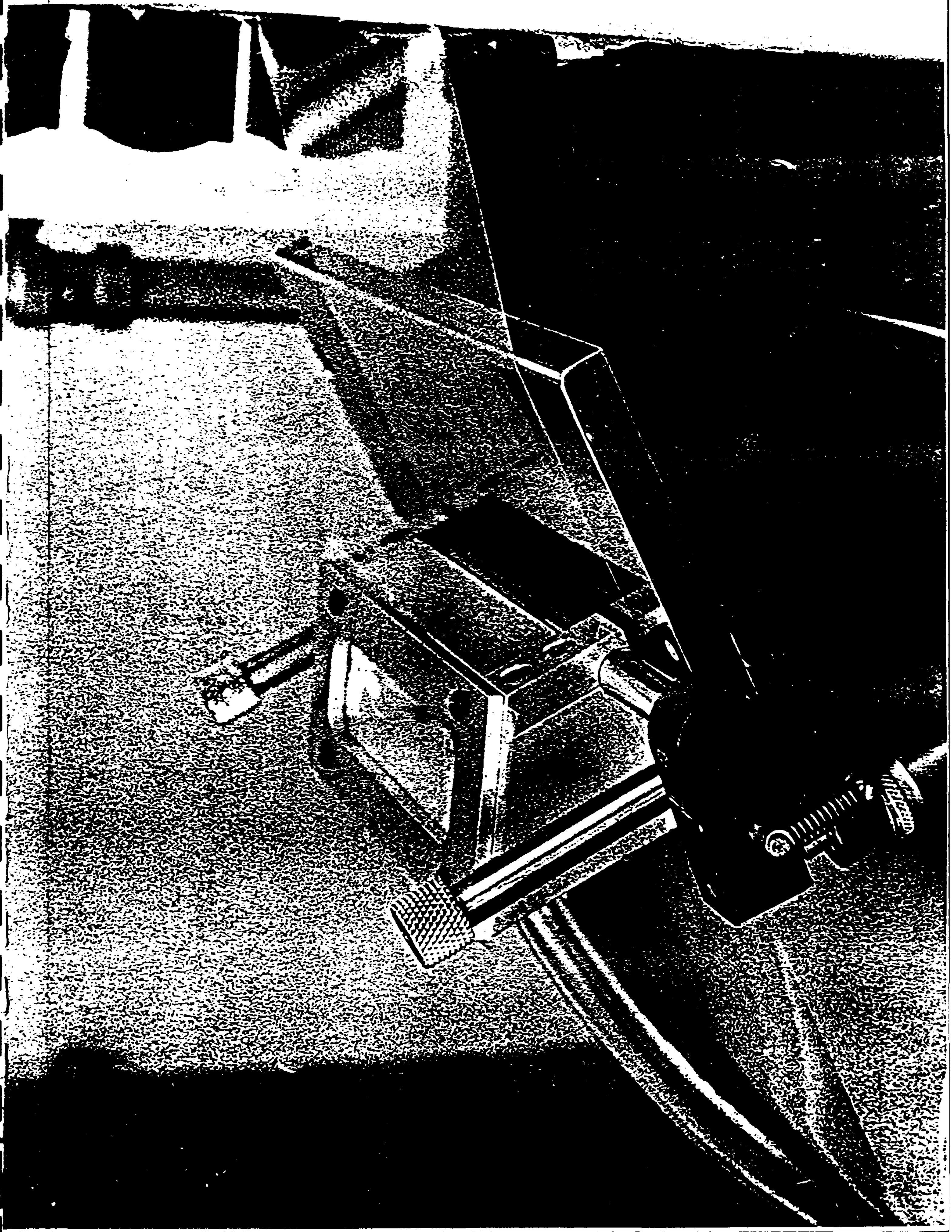
Surface Protected

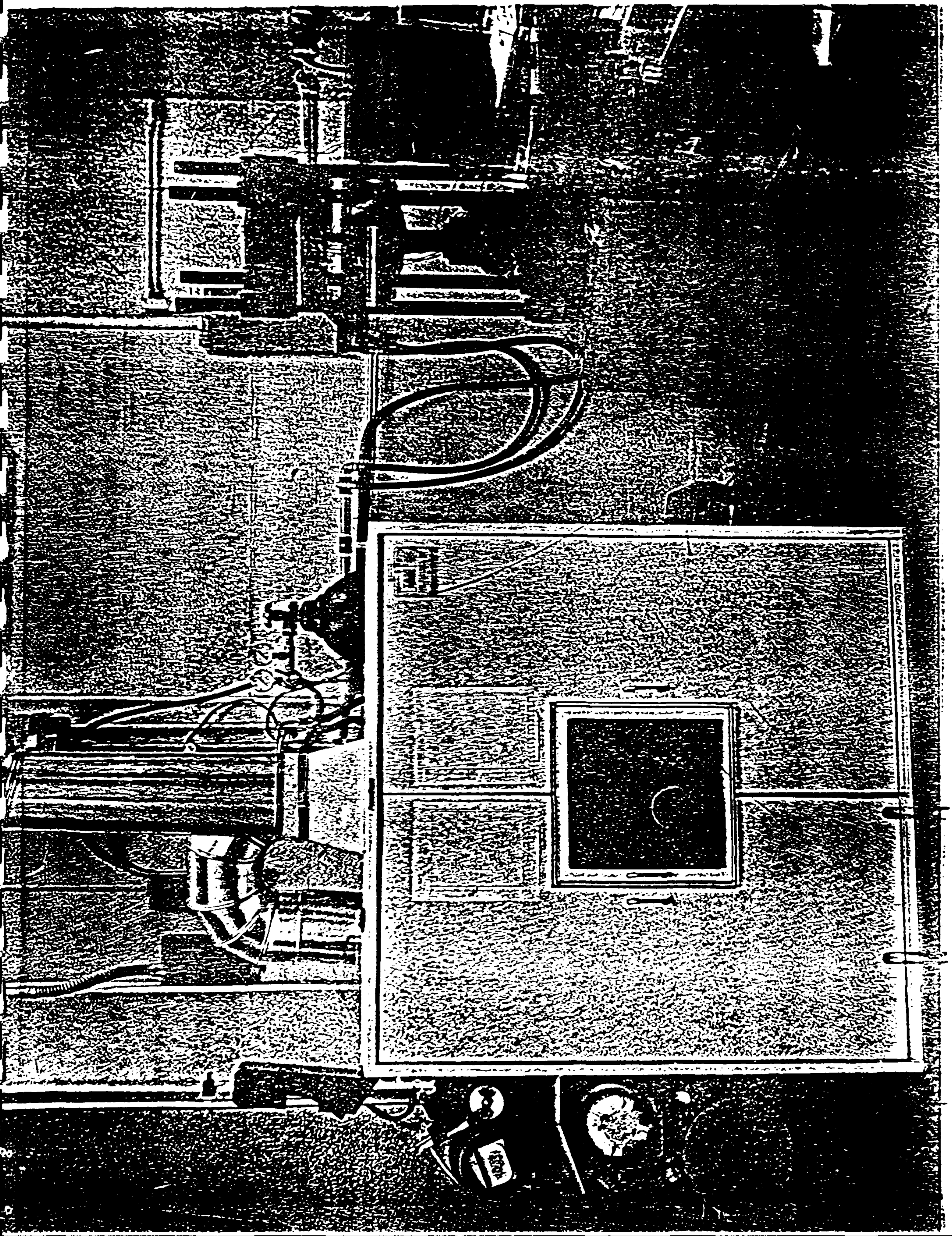


Toughened

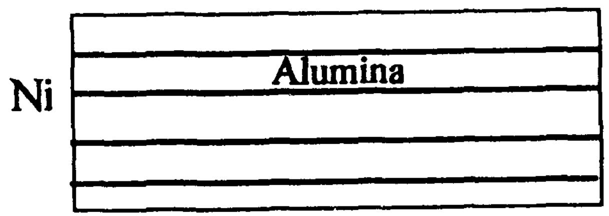

OBJECTIVES
SELECTION OF MATERIALS
LAMINATE DESIGN (ELASTICITY THEORY)
IS DESIGN COMPATIBLE WITH MATERIALS?
NO
YES
TAPE CASTING
LAMINATION
BINDER BURNOUT
IS LAMINATE CRACK-FREE?
NO
YES
HOT PRESSING
PROPERTY MEASUREMENTS
ARE OBJECTIVES MET?
NO
YES
SELECT DESIGN


CELLULOSE ACETATE SHEET
DOCTOR BLADE
DRYING ZONE
SLIP
STORAGE ROLL FOR CELLULOSE ACETATE SHEET

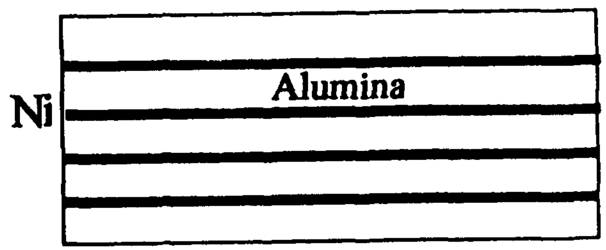




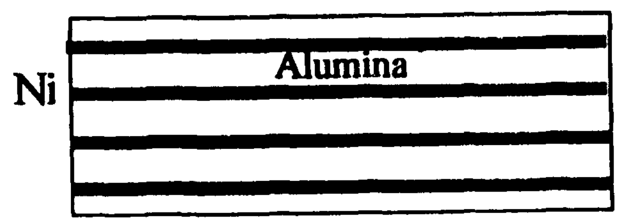
SAMPLE DESIGNATION



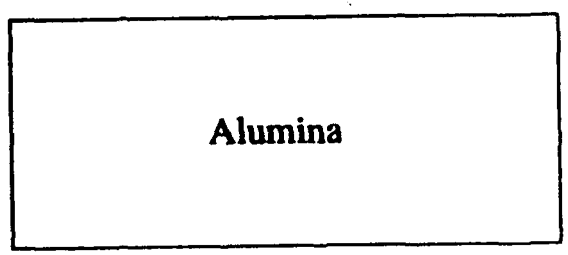
Ni(.125)



Ni (.180)



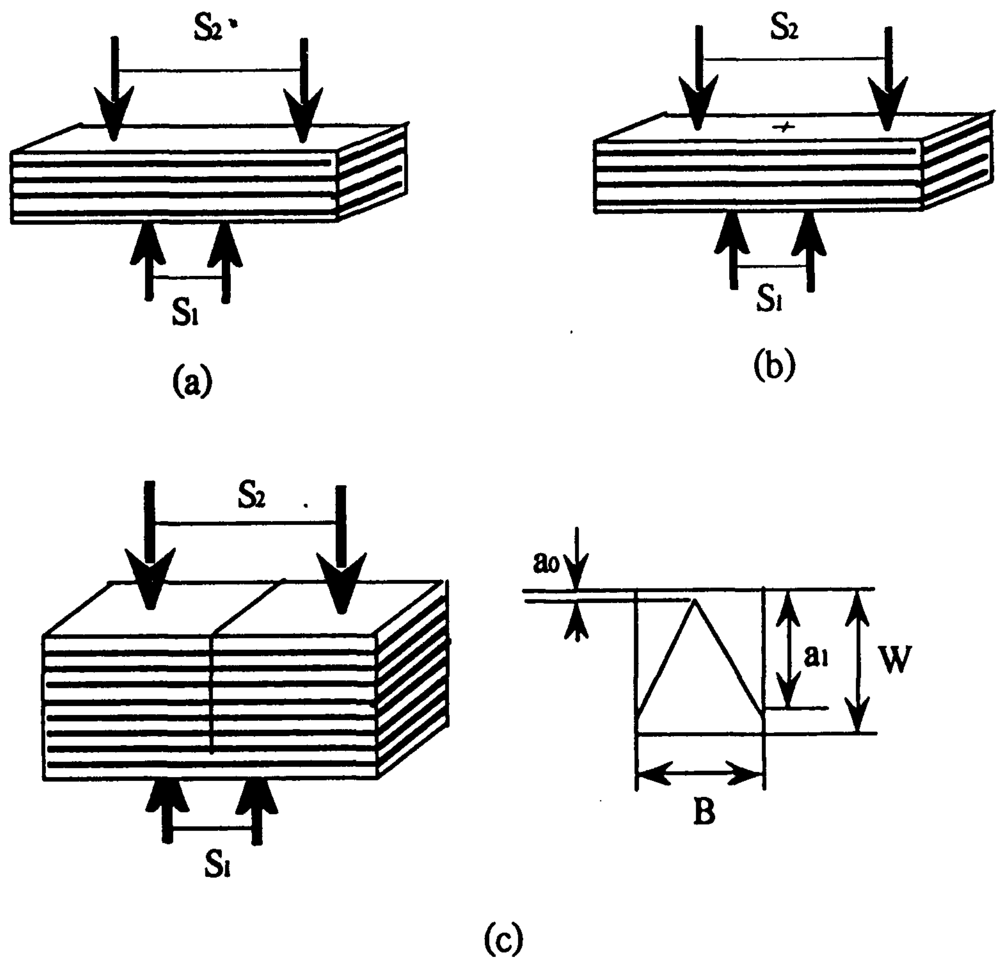
Ni (.240)



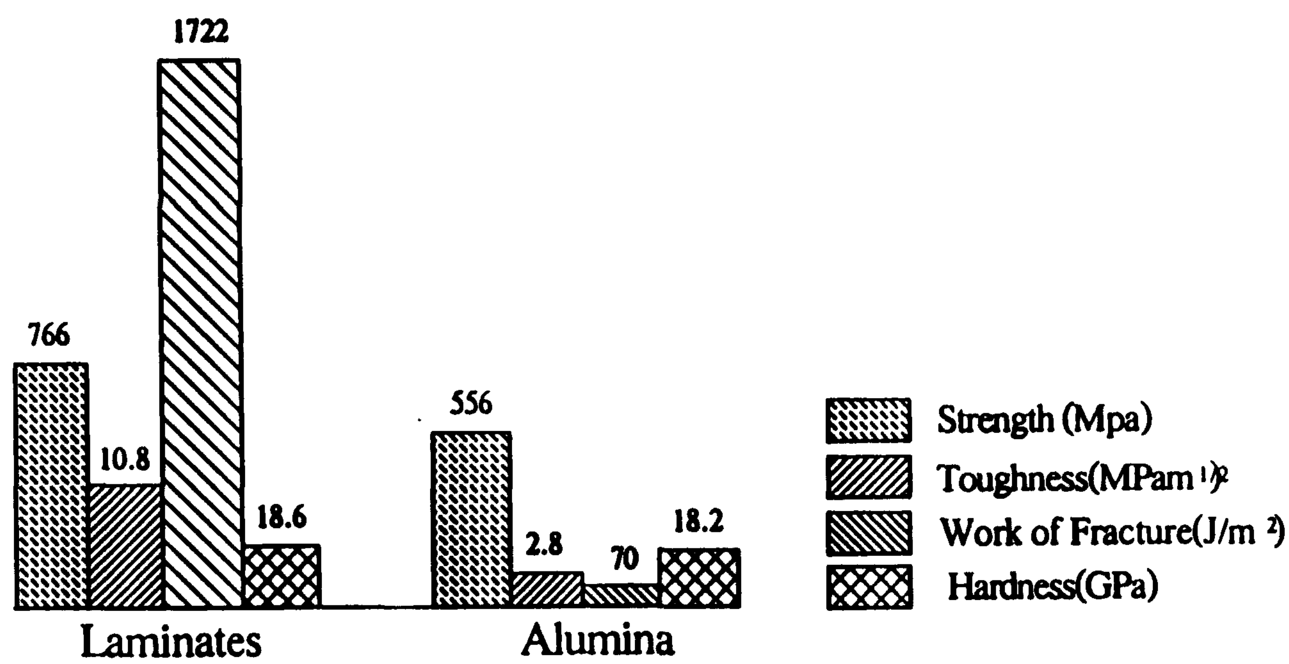
Al2O3

All external layers are .22 mm and internal layers are .30 mm for alumina

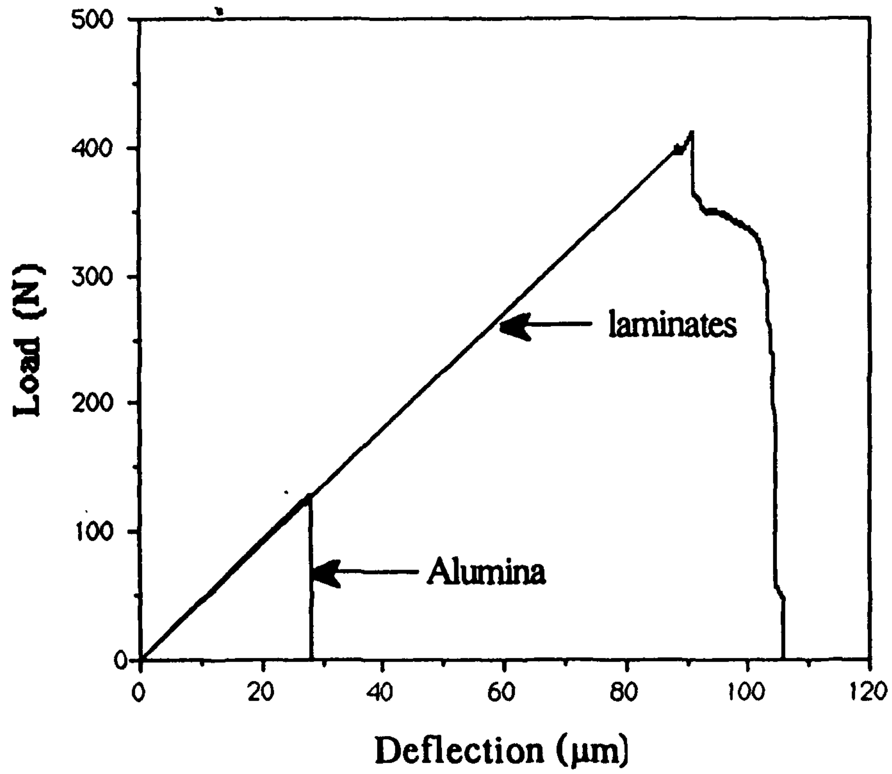
DIFFERENT TESTS ARE REQUIRED TO EVALUATE COMPOSITES



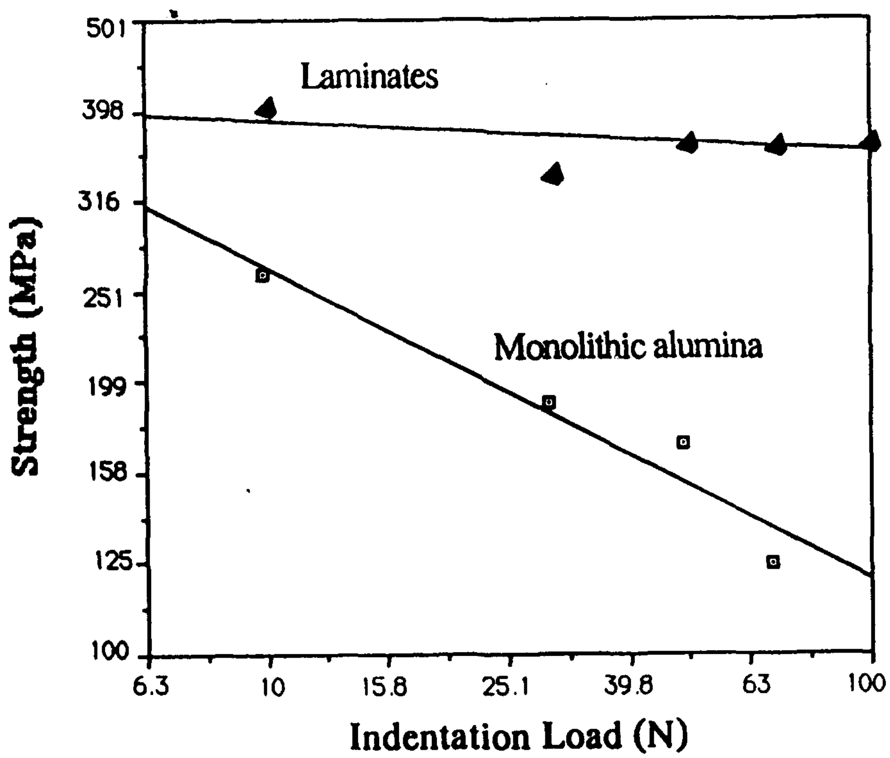
Improved Mechanical Properties



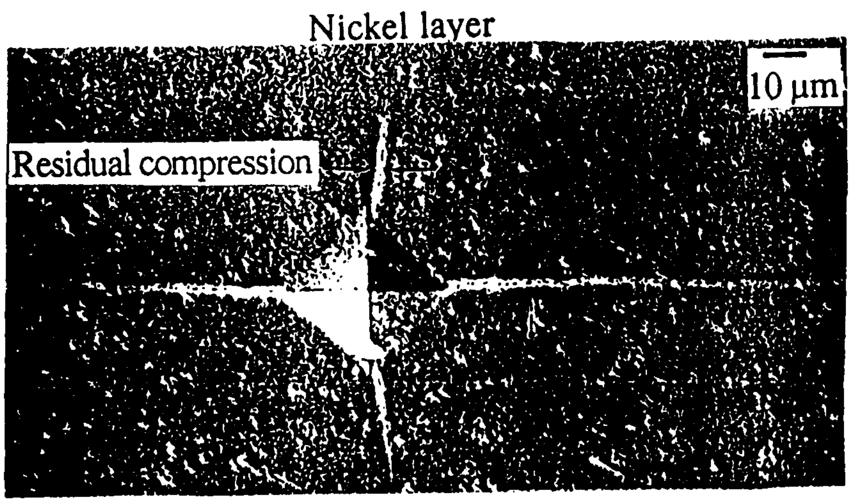
LAMINATES SHOW INCREASED TOUGHNESS OVER MONOLITHICS

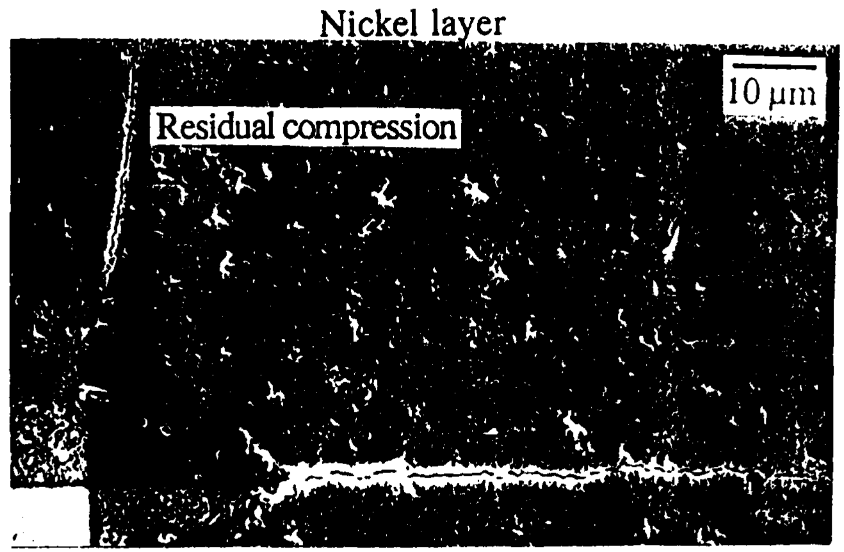


STRENGTH NEARLY INDEPENDENT OF CRACK SIZE FOR LAMINATES

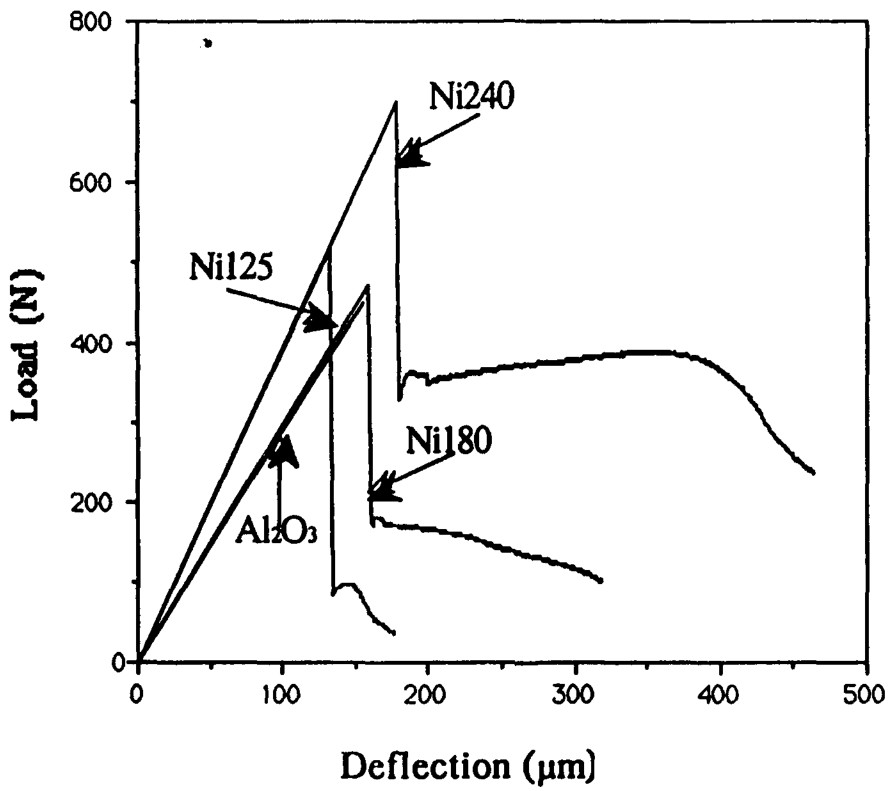


RESIDUAL COMPRESSIVE STRESSES IMPEDE CRACK DEVELOPMENT

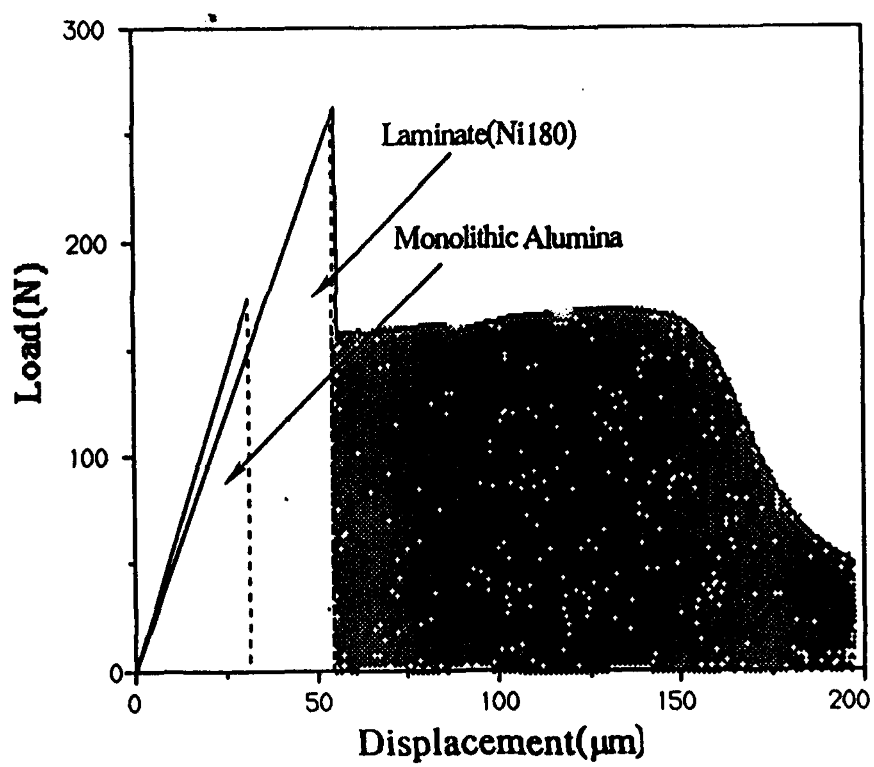




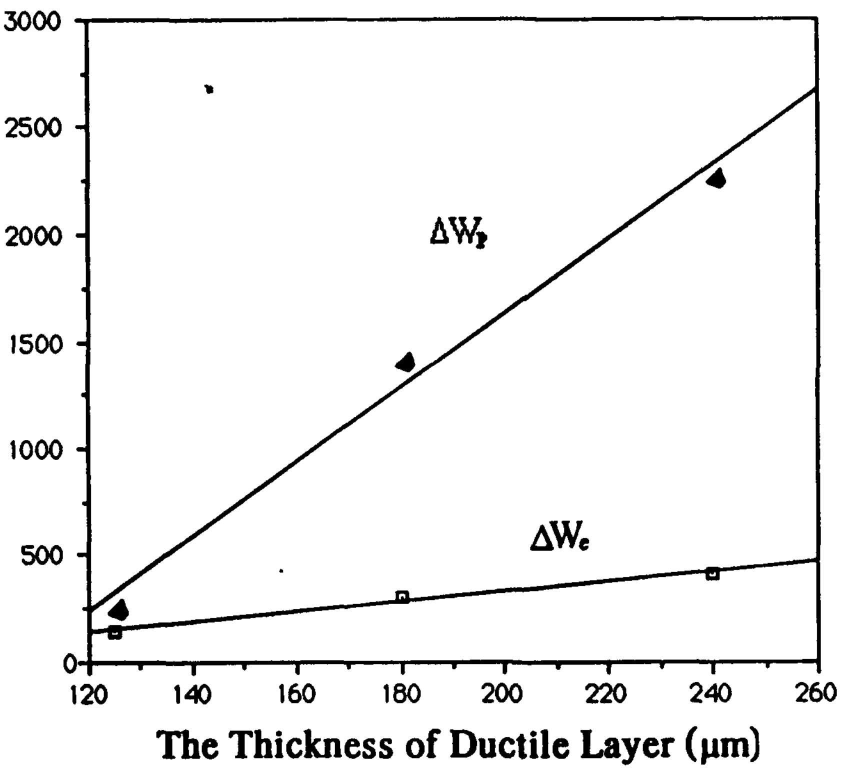
DUCTILITY INCREASES WITH INCREASING THICKNESS OF METAL LAYER



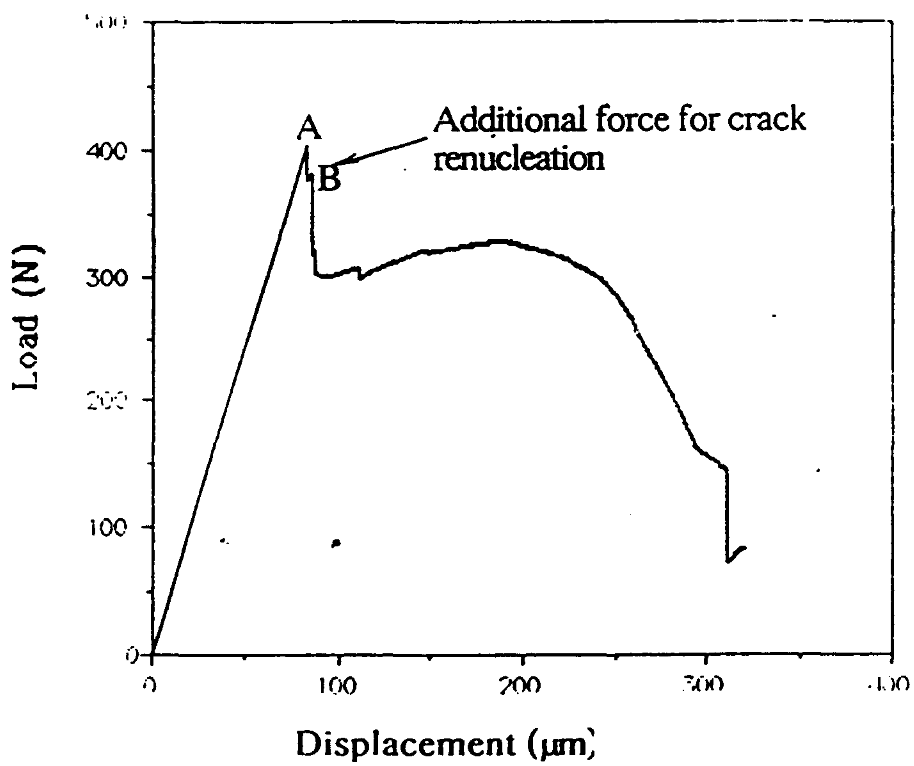
APPARENT TOUGHNESS INCREASES DUE TO ELASTIC AND PLASTIC PROCESSES



WORK OF FRACTURE INCREASES WITH INCREASE IN THICKNESS



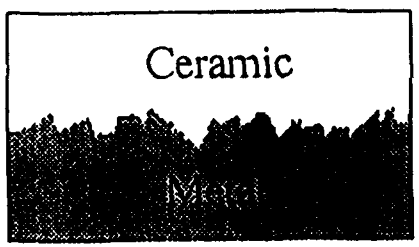
a. Scanning electron micrograph of the fracture surface of a laminate illustrates the crack renucleation created beneath the ductile layer at B, after fracture started at A.



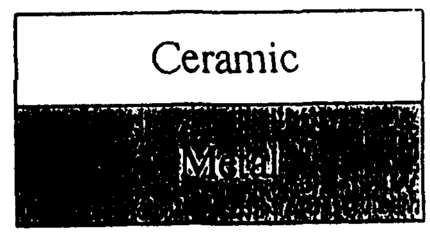
b. Load-displacement curve shows an interruption at B due to crack renucleation during load drop.

Figure 13. Scanning electron micrograph and graph illustrate crack renucleation in a laminate.

Bonding Strength of Ceramic/Metal Depends on Total Contact Area of the Interface

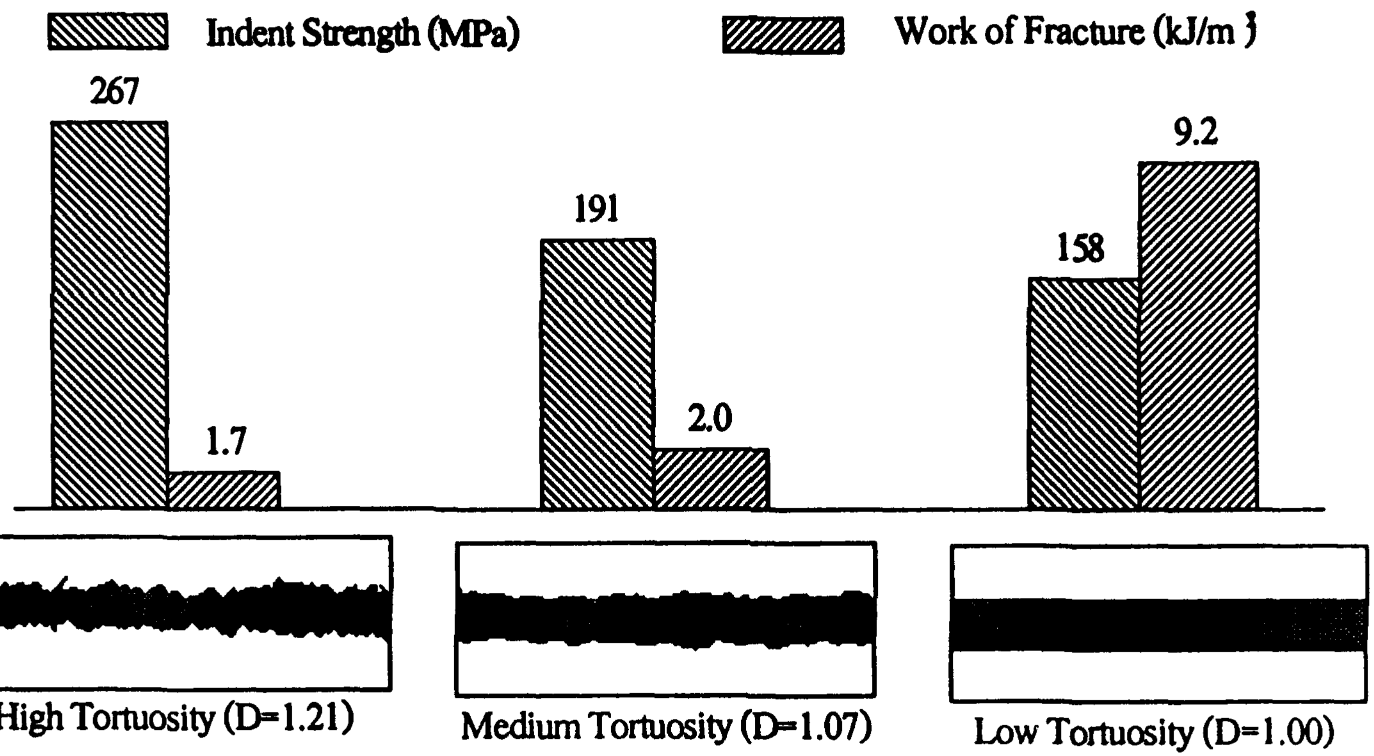


Larger Total Contact Area
(High Tortuosity)

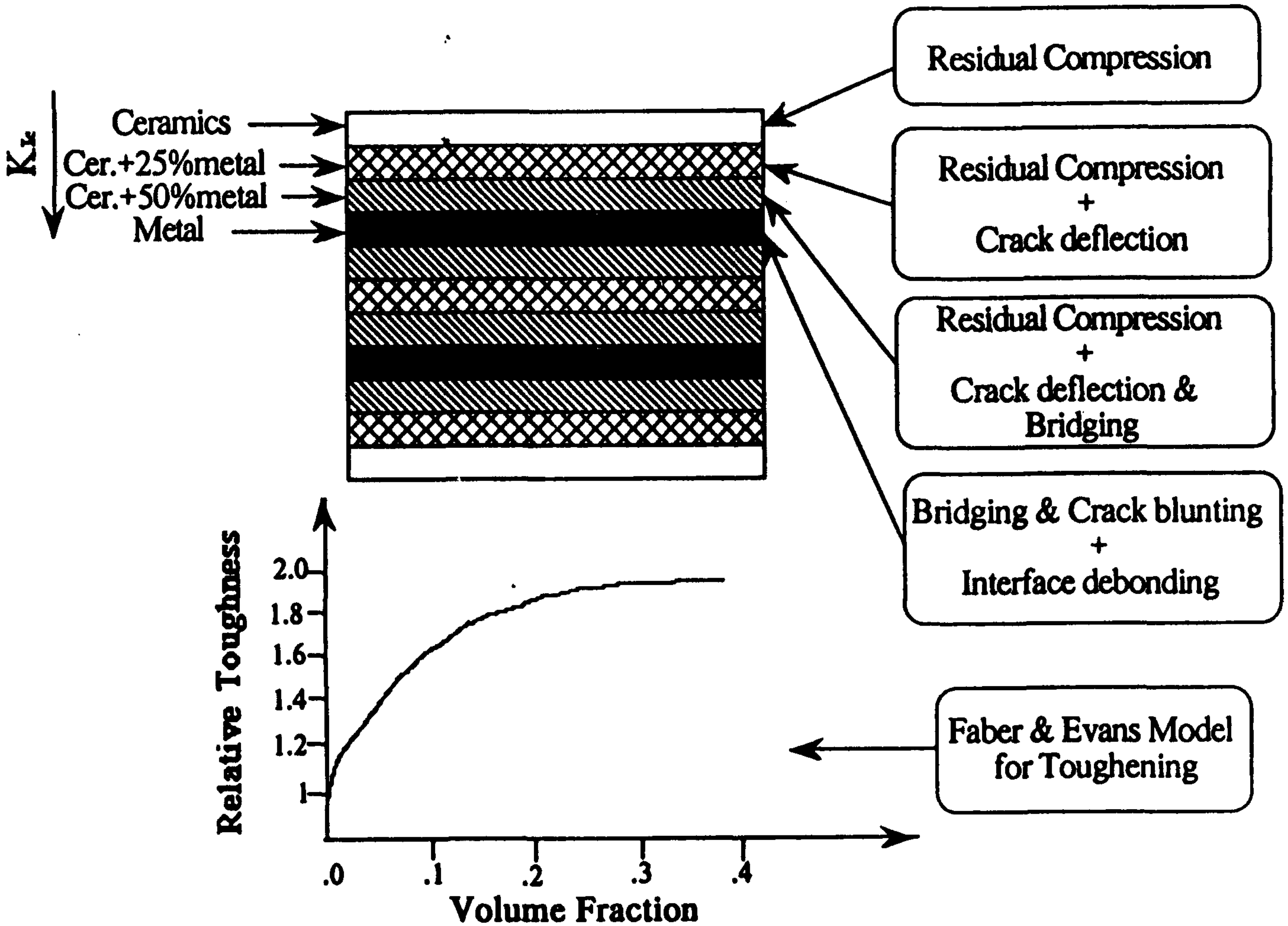


Small Total Contact Area
(Low Tortuosity)

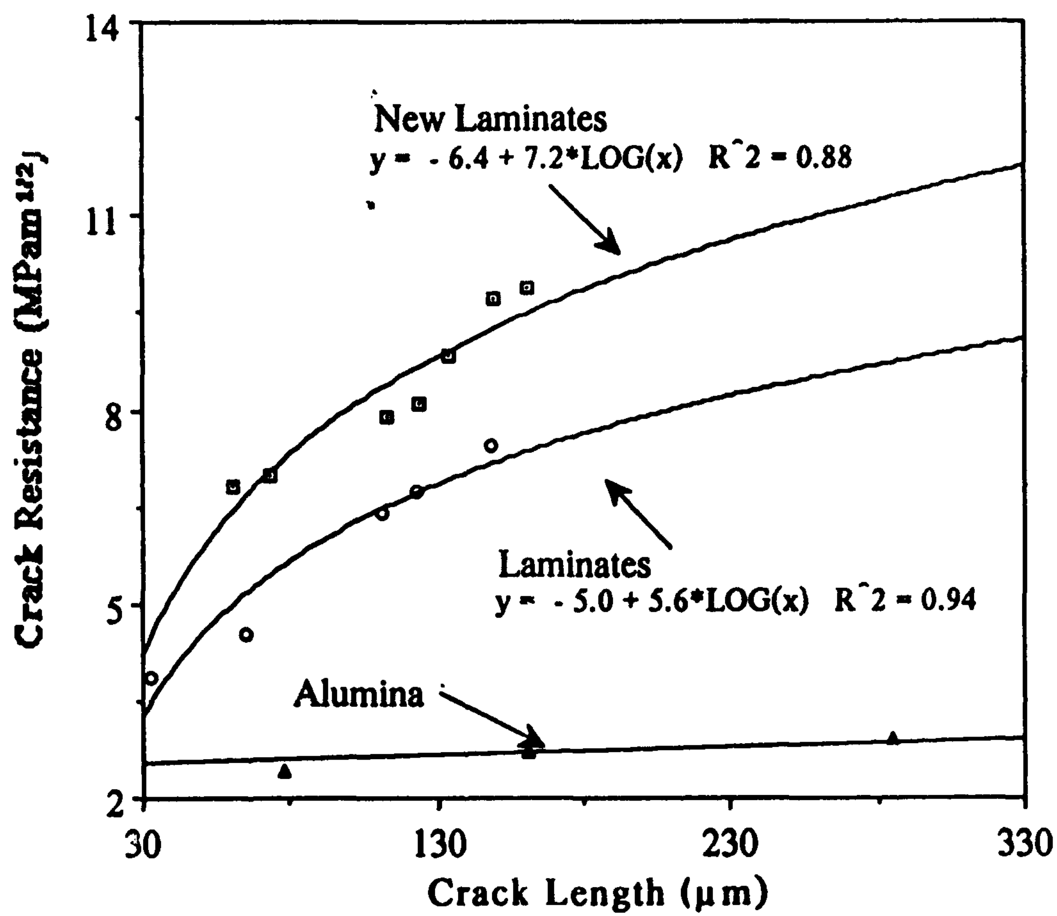
Interface Tortuosity Controls Strength And Toughness



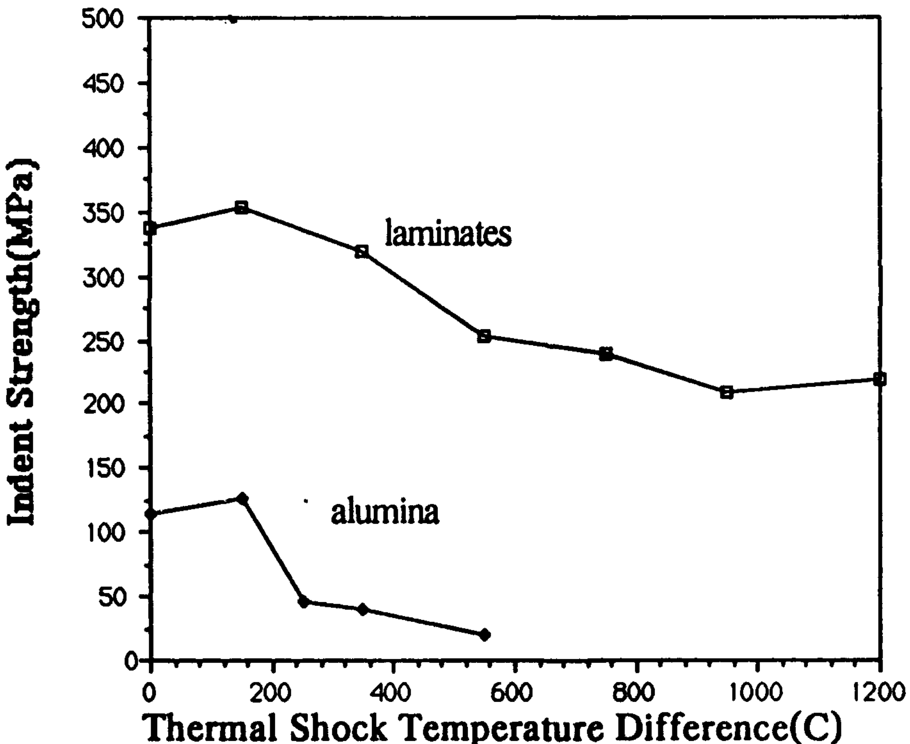
Graded Composites Are Designed To Improve Toughness



R-Curve Behavior Improved By Designing Laminates



LAMINATES SHOW DAMAGE TOLERANCE



* All samples were quenched into room temperature water
** All samples with a 12 Kg load indentation

CONCLUSIONS - Multilayered Design Offers New Potential

I. Multilayer Laminate Design Offers the Potential of New Materials.

II. Tapecasting Offers the Potential Of Commercial Production.

III. Ceramic/Metal Composites Offer the Potential of Crack Size Independent Strength and Damage Tolerant Design.